



Iron-Group and Amorphous Alloys: Promising Electrocatalysts For Alkaline Her - A Review

Shaik Mohammad Azam, Ch. Maneesha, B. Dilip Kumar*

Department of Chemical Engineering, JNTUA College of Engineering (Autonomous), Jawaharlal Nehru Technological University Anantapur (JNTUA), Ananthapuramu, Andhra Pradesh, 515002, India. * Corresponding Author-Email:

(Received: 07 January 2024

Revised: 12 February 2024

Accepted: 06 March 2024)

KEYWORDS

Electrocatalysts,
Hydrogen
evolution reaction,
Overpotential,
Electrodeposition,
Alloying, Alkaline
solutions

ABSTRACT:

The drive for efficient and sustainable hydrogen production has prompted research into creating more effective electro-catalysts. By carefully synthesizing metal composite/alloy films through various deposition techniques, it's possible to fine-tune their electro-catalytic characteristics. This review explores the development and properties of promising electrocatalysts, particularly those based on iron-group elements (iron, nickel, or cobalt). Amorphous alloys, with their unique combination of electrochemical, mechanical, and corrosion-resistant properties, have attracted significant research interest. The review highlights molybdenum and phosphorus as especially effective elements for creating amorphous alloys, focusing on their co-deposition technique. Additionally, other metal groups like pure metals and rare-earth elements in alloyed composite forms are discussed. Finally, the review emphasizes the use of electrodeposition methods for preparing these alloys, particularly relevant for applications in the chlor-alkali industry.

1. Introduction

Hydrogen is gaining traction as a potential energy carrier for a low-carbon future, offering a clean alternative to traditional fossil fuels. Electrochemical hydrogen generation by electrocatalysis has received considerable interest as a cost-effective and environmentally healthy technique of producing hydrogen from water.¹ The employment of catalysts to enhance electrochemical processes at the electrode-electrolyte interface is known as electrocatalysis. Designing and developing efficient and long-lasting electrocatalysts is critical for sustainability of hydrogen generation.

The hydrogen evolution reaction (HER) plays a critical role in bridging the gap between fundamental science and practical applications. Early research on hydrogen adsorption, a key step before HER, laid the foundation for modern electrochemistry. Meanwhile, the long-held dream of water splitting – using electricity to separate water into its components – has gained renewed urgency in recent decades. The rise of renewable energy sources and the promise of clean, fuel cell-powered technologies have made HER a key research area.

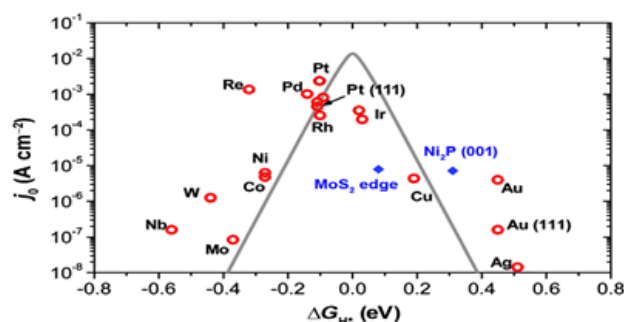


Fig 1 : HER Activity vs. Hydrogen Adsorption Energy (Volcano Plot)²

2. Metals

Volcano plot, a key concept in electrocatalysis, suggests that optimal HER activity hinges on a specific balance in hydrogen (H) adsorption energy³. This implies that most pure metals, except for a few expensive noble metals, struggle to efficiently catalyze HER. To overcome this limitation and utilize cheaper metals, researchers turn to alloying, which combines multiple metals with varying H-bonding strengths⁴. Alloying offers a two-pronged approach: strong M-H bonds on one metal component can facilitate initial H adsorption, while weaker M-H bonds on another component can promote H₂ formation and release. The prevailing theory suggests that strong M-H bonds initiate H adsorption, followed by surface diffusion of the adsorbed H atoms to sites with weaker



M-H bonds. These weaker bonds then readily release H₂ molecules from the electrode surface.

Similar to the influence of size differences in noble metal alloys, introducing a metal of varying size can alter the catalyst's lattice structure, potentially creating more active sites for HER⁵. While corrosion is less of a concern during HER compared to anodic reactions where metal oxides promote dissolution, electrochemical instability remains a significant challenge for active metal electrocatalysts. Research on active metal alloys for HER prioritizes two key improvements: enhancing electrochemical stability and maximizing active sites. Porosity engineering is a promising approach to achieve both goals⁵.

While many electrocatalyst materials struggle in alkaline media, metal alloys stand out as particularly promising candidates for the hydrogen evolution reaction (HER). Their unique properties make them well-suited for this challenging environment⁶. While most HER research focuses on acidic environments, alkaline media holds significant value for fuel cell applications. However, the presence of hydroxide anions adds complexity to the HER mechanism in alkaline media, creating an area of ongoing research.

Research on metallic alloy electrocatalysts can pave the way for the development of new types of electrocatalysts based on transition metal compounds. Interestingly, alloying approaches can even incorporate various anions like phosphorus (P) into the structure. These anion-containing alloys share similarities with their corresponding transition metal compounds. For example, a NiP_x alloy exhibits properties akin to a Ni₂P compound, as we'll explore further.

3. Metal phosphides

Since the 1990s, NiP_x alloys have been gaining traction as promising candidates for HER electrocatalysis⁷⁻⁹. Computational studies hinted at a metallic-like behavior of Ni₂P during HER¹⁰. This concept gained ground with recent experiments confirming metal phosphides as a viable option¹¹⁻¹². This promising finding has fueled a surge in research on transition metal phosphides (TMPs) as HER electrocatalysts, particularly in the last decade (2010-present)¹²⁻³². TMPs hold significant advantages over traditional materials like metal sulfides. For instance, FeP/CC electrocatalysts exhibit overpotentials comparable to Pt, the benchmark material³³. Unlike MoS₂ where activity is restricted to

reactive edges, TMPs demonstrate activity throughout their entire structure³³. Additionally, their metallic properties may be intrinsic to their crystal structure, avoiding the challenges of unstable phases encountered in materials like MoS₂.

Despite their initial promise, transition metal phosphides still face hurdles before widespread practical use. Their negatively charged phosphorus sites make them reactive, but this can also lead to the development of a passive layer on the surface. This acts as a barrier, completely hindering the electrocatalytic reaction. Additionally, our understanding of both the electrochemical and materials chemistry of transition metal phosphides lags behind that of other similar transition metal compounds discussed earlier. To bridge this gap, researchers need a deeper knowledge of how these materials behave within an electrochemical cell.

Table 1 compares the performance of nickel phosphide (Ni₂P) catalysts for the hydrogen evolution reaction (HER) under different synthesis conditions. These catalysts were all tested in 0.5 M sulfuric acid (H₂SO₄). Notably, Table 1 highlights the performance of Ni₂P nanoparticles, the first experimentally studied Ni₂P HER catalysts, synthesized using a reaction between trioctylphosphine (TOP) and nickel(II) acetylacetonate at 320°C for 2 hours. Since then, researchers have developed several methods to create Ni₂P nanoparticles in a liquid suspension (colloidal).

Table 1. Compilation of HER Performance Metrics for Various Nickel Phosphide Catalysts Synthesized under Different Conditions and Evaluated in 0.5 M H₂SO₄.

Material	Tafel slope (mV dec ⁻¹)	Exchange current density (A cm ⁻²)	Loading density (mg cm ⁻²)	Ref
Ni ₂ P NPs/Ti	46	3.3×10 ⁻⁵	1.0	33
Ni ₂ P/CN T	53	5.37×10 ⁻⁵	-	34
NiP ₂ NS/CC	51	2.60×10 ⁻⁴	4.3	35



Ni ₁₂ P ₅ /C NT	56	7.10×10^{-5}	0.75	36
Ni ₂ P/GC E	84	2.90×10^{-6}	0.15	37
MOF- derived Ni ₁₂ P	270	4.50×10^{-5}	0.35	38
Ni ₅ P ₄	46.1	2.75×10^{-4}	0.15	39

For the initial HER catalyst studies, the chosen synthesis method was the one reported by Tracy and colleagues. This method was selected because it offers a simple one-pot reaction to produce a uniformly sized and phase-pure (single-phase) Ni₂P nanocrystals. Ni₂P nanoparticles were applied to titanium foil substrates to create working electrodes for HER testing. These electrodes underwent an annealing process at 450°C in a hydrogen and nitrogen mixture (5% H₂ / 95% N₂). This step removes organic ligands that initially coated the nanoparticles. The resulting films of Ni₂P nanoparticles wanted a low overpotential of only -116 mV to get a current density of -10 mA cm⁻² in a strong electrolyte (0.5 M H₂SO₄). These Ni₂P electrodes also demonstrated good stability and efficient hydrogen production over a sustained 2-hour period.

Similar promising results were obtained by Hu and colleagues. Their Ni₂P nanoparticles, synthesized through a reaction among sodium hypophosphite and nickel chloride hexahydrate (NiCl₂·6H₂O), displayed excellent activity and stability in electrolyte solutions. They achieved results of approximately -125 and -230 mV at -10 mA cm⁻² in both conditions, respectively. These results put Ni₂P in the company of top non-precious metal HER electrocatalysts reported at that time, rivaling other materials like MoS₂, NiMoN, MoB, and Mo₂C. Beyond the initial examples, research has shown similar promise for a broad range of Ni₂P materials.

- Sun et al. fabricated Ni₂P nanoparticle films through a low-temperature process. They achieved this by phosphiding pre-deposited nickel hydroxide precursors. These films performed competitively, requiring around 130 mV overpotential at -10 mA cm⁻² current density in 0.5 M H₂SO₄. Notably, they also exhibited

remarkable hydrogen production for a period of 15 hours.⁴²

- Liu et al. noted similar activity with Ni₂P nanoparticles deposited on multi-walled carbon nanotubes (Ni₂P/CNT). These composite catalysts attain an overpotential of around -124 mV only with -10 mA cm⁻². The resulting Ni₂P/CNT was then deposited onto glassy carbon electrodes for testing.⁴³

The introduction of a versatile and scalable method for synthesizing metal phosphide electrodes. This method involves using commercially available metal foils via a vapor phase reaction with many organophosphine compounds. The results displayed remarkable HER performance. For example, Ni₂P electrodes needed overpotentials of around -128 mV in 0.5 M H₂SO₄ and -183 mV in 1 M KOH for HER. Furthermore, we successfully applied this strategy to thin metal films deposited through evaporation. This method allows for the deposition of conformal metal phosphide coatings, well-suited for diverse substrates. This includes promising photocathode materials like highly doped silicon, opening doors for advancements in photocatalysis. While these Ni₂P thin films on silicon had low material loadings and surface areas, they still exhibited moderate HER, attaining an overpotential of around -240 mV.

Researchers have achieved significant improvements in Ni₂P's HER performance by incorporating it into composite materials with carbon or using 3D electrode designs.

Carbon Composites: For example, Wang et al. created carbon-encapsulated Ni₂P nanoparticles by transforming Ni-containing precursors with hydrogen gas. These composites exhibited superior HER, attaining only an overpotential of -87 mV. The improved results are due to increased nanoporosity within the material, This approach improves the utilization of active sites, resulting in a significant increase in catalytic activity.

3D Electrodes: Du et al. reported exceptional HER activity with a 3D electrode design. They coated a three-dimensional graphene/nickel foam structure. This electrode achieved a very low overpotential of -55 mV. The high performance is likely due to the increased number of active sites available due to the large surface area of the porous electrode, along with improved movement of ions and electrons within the material. It's important to note that the activity of this 3D electrode



was normalized to a flat surface area for comparison, despite its inherently porous nature.⁴⁵

Undeterred by the diverse approaches to Ni_2P synthesis, size, shape, and supporting materials, most studies show a similar average overpotential of -125 mV for Ni_2P HER catalysts. The crystal structure and bonding within Ni_2P can significantly impact its catalytic properties for HER. Studies have explored how different nickel phosphide phases influence HER activity.

Impact of Nickel Phosphide Phases: Liu et al. compared the performance of various phases (Ni_{12}P_5 , Ni_2P , and Ni_5P_4) under similar conditions (Figure 1). They found that Ni_5P_4 displayed superior HER activity compared to the other two phases. The improved performance is linked to the way nickel and phosphorus atoms interact in Ni_5P_4 . Nickel atoms have a slightly positive charge, and the arrangement of phosphorus atoms strengthens their collaboration, leading to better activity. Nevertheless, it's important to note that variations in particle size, morphology, and surface area between the samples could also contribute to the observed differences in activity (Figure 1)⁴¹.

These findings, corroborated by similar research, strongly suggest that the metal-to-phosphorus ratio plays a critical role in the hydrogen evolution reaction (HER) performance of metal phosphides. Materials with a higher phosphorus content often exhibit better HER activity. For instance, reports on NiP_2 nanosheets, which have a high phosphorus content, demonstrate exceptional HER with an overpotential of only -75 mV. This mechanism suggests a cooperative interaction between phosphorus and nickel atoms, implying a dependence on the ratio of phosphorus to nickel.

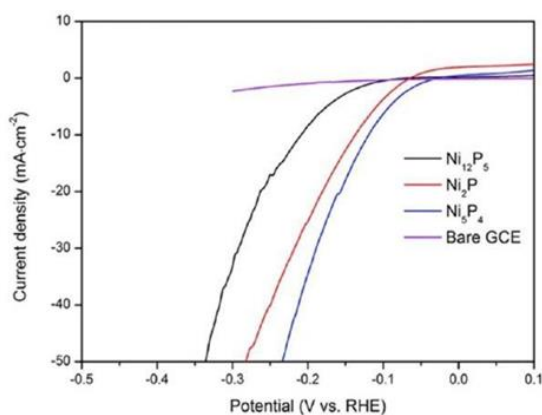


Figure 1: Linear sweep Voltammogram of Nanostructured Nickel phosphide phases.

4. Summary

Efficient and affordable HER electrocatalysts are key to unlocking the full potential of clean hydrogen for a sustainable energy future. HER holds immense potential for production Green hydrogen, a key player in sustainable energy solutions. Currently, platinum (Pt) reigns supreme as the best effective HER catalyst. However the limitations associated with practical use, such as the need for carbon support and potential stability issues, make it an impractical choice for large-scale hydrogen production. Pt-based catalysts often require carbon support, which can raise operational costs due to potential mechanical degradation over time. Portable applications for HER, for example in fuel cells for powering devices, would necessitate Pt recycling strategies due to its scarcity. Therefore, the focus of research has shifted towards exploring alternative electrocatalysts that are both inexpensive and practical. Nickel phosphides (NiPx) have emerged as a frontrunner in this category, offering a promising alternative to Pt for HER.

5. Outlook

Despite the promising results, more advanced research is required to completely realize the potential of NiPx for HER applications:

Carbon Catalyst Support: While highly desirable, a high surface area carbon support isn't the only factor for optimal performance. Even platinum (Pt), the best-known HER catalyst, requires a suitable carbon support to achieve its full potential (beyond just a low overpotential). This highlights the importance of the carbon support's physical and chemical structure in influencing HER activity.

Alternative HER Catalysts: The search for practical alternatives to expensive Pt catalysts has led researchers to explore compounds like transition metals. These materials can be sulfides, selenides, phosphides, or carbides, offering a wider range of options with potentially lower costs.

Core/Shell Design for Enhanced Performance: A promising approach for boosting the available active sites in HER electrocatalysts is the core/shell architecture. This design allows for a targeted placement of the active material, maximizing its utilization while maintaining other desirable properties for practical applications. While increasing active sites on the edges of 2D layered structures shows promise for the hydrogen evolution reaction (HER), the overall structure may not be practical for large-scale production or real-world



applications. The core/shell approach offers a more practical solution.

Doping the carbon support with foreign elements is a powerful technique for enhancing the performance of HER electrocatalysts. This method strategically manipulates the charge distribution within the carbon material, resulting in the creation of a higher number of active catalytic sites.

References

1. Liu, G.; Hou, F.; Wang, X.; Fang, B. Stainless Steel-Supported Amorphous Nickel Phosphide/Nickel as an Electrocatalyst for Hydrogen Evolution Reaction. *Nanomaterials* 2022, 12, 3328. <https://doi.org/10.3390/nano12193328>
2. Tek, Gökçen. (2021). Time-resolved infrared spectroscopy of small molecules on heterogeneous metal surfaces. 10.13140/RG.2.2.30750.82245.
3. Parsons R. The rate of electrolytic hydrogen evolution and the heat of adsorption of hydrogen. *Trans Faraday Soc* 1958;54:1053. <http://dx.doi.org/10.1039/tf9585401053>.
4. Miles MH. Evaluation of electrocatalysts for water electrolysis in alkaline solutions. *J Electroanal Chem Interf Electrochem* 1975;60:89e96. [http://dx.doi.org/10.1016/S0022-0728\(75\)80205-1](http://dx.doi.org/10.1016/S0022-0728(75)80205-1).
5. Xiao Y, Liu Y, Tang Z, Wu L, Zeng Y, Xu Y, et al. Porous NiCoFe alloys as cathode materials for the hydrogen evolution reaction. *RSC Adv* 2016;6:51096e105. <http://dx.doi.org/10.1039/c6ra07316f>.
6. Saha A, Raghavachari K. Hydrogen evolution from water through metal sulfide reactions. *J Chem Phys* 2013;139:204301. <http://dx.doi.org/10.1063/1.4830096>.
7. Ranaweera CK, Wang Z, Alqurashi E, Kahol PK, Dvornic PR, Gupta BK, et al. Highly stable hollow bifunctional cobalt sulfides for flexible supercapacitors and hydrogen evolution. *J Mater Chem A* 2016;4:9014e8. <http://dx.doi.org/10.1039/c6ta03158g>.
8. Dai X, Liu M, Li Z, Jin A, Ma Y, Huang X, et al. Molybdenum polysulfide anchored on porous Zr-Metal organic framework to enhance the performance of hydrogen evolution reaction. *J Phys Chem C* 2016;120:12539e48. <http://dx.doi.org/10.1021/acs.jpcc.6b02818>.
9. Kwon DH, Jin Z, Shin S, Lee W, Min Y. A comprehensive study on atomic layer deposition of molybdenum sulfide for electrochemical hydrogen evolution. *Nanoscale* 2016;8:7180e8. <http://dx.doi.org/10.1039/c5nr09065b>
10. Liu P, Rodriguez JA. Catalysts for hydrogen evolution from the [NiFe] hydrogenase to the Ni₂P(001) Surface: the importance of ensemble effect. *J Am Chem Soc* 2005;127:14871e8. <http://dx.doi.org/10.1021/ja0540019>.
11. Xu Y, Wu R, Zhang J, Shi Y, Zhang B. Anion-exchange synthesis of nanoporous FeP nanosheets as electrocatalysts for hydrogen evolution reaction. *Chem Commun* 2013;49:6656e8. <http://dx.doi.org/10.1039/c3cc43107j>.
12. Shi Y, Zhang B. Recent advances in transition metal phosphide nanomaterials: synthesis and applications in hydrogen evolution reaction. *Chem Soc Rev* 2016;45:1529e41. <http://dx.doi.org/10.1039/c5cs00434a>.
13. Xiao P, Chen W, Wang X. A review of phosphide-based materials for electrocatalytic hydrogen evolution. *Adv Energy Mater* 2015;5:1500985. <http://dx.doi.org/10.1002/aenm.201500985>.
14. Gao S, Liu Y, Li G, Guo Y, Zou Y, Zou X. General urea-assisted synthesis of carbon-coated metal phosphide nanoparticles for efficient hydrogen evolution electrocatalysis. *Electrochim Acta* 2016;199:99e107. <http://dx.doi.org/10.1016/j.electacta.2016.03.104>.
15. Zhou D, He L, Zhu W, Hou X, Wang K, Du G, et al. Interconnected urchin-like cobalt phosphide microspheres film for highly efficient electrochemical hydrogen evolution in both acidic and basic media. *J Mater Chem A* 2016;4:10114e7. <http://dx.doi.org/10.1039/c6ta03628g>.
16. Feng Y, Yu X, Paik U. Nickel cobalt phosphides quasi-hollow nanocubes as an efficient electrocatalyst for hydrogen evolution in alkaline solution. *Chem Commun* 2016;52:1633e6. <http://dx.doi.org/10.1039/c5cc08991c>.
17. Deng C, Ding F, Li X, Guo Y, Ni W, Yan H, et al. Templated preparation of a three-dimensional molybdenum phosphide sponge as a high performance electrode for hydrogen evolution. *J Mater Chem A* 2016;4:59e66. <http://dx.doi.org/10.1039/c5ta05453b>.
18. Wang D, Zhang D, Tang C, Zhou P, Wu Z, Fang B. Hydrogen evolution catalyzed by cobalt-promoted molybdenum phosphide nanoparticles.



- Catal Sci Tech 2016;6:1952e6. <http://dx.doi.org/10.1039/c5cy01457c>.
19. Pan Y, Lin Y, Chen Y, Liu Y, Liu C. Cobalt phosphide-based electrocatalysts: synthesis and phase catalytic activity comparison for hydrogen evolution. *J Mater Chem A* 2016;4:4745e54. <http://dx.doi.org/10.1039/c6ta00575f>.
20. Reddy DA, Choi J, Lee S, Kim Y, Hong S, Kumar DP, et al. Hierarchical dandelion-flower-like cobalt-phosphide modified CdS/reduced graphene oxide-MoS₂ nanocomposites as a noble-metal-free catalyst for efficient hydrogen evolution from water. *Catal Sci Tech* 2016;6:6197e206. <http://dx.doi.org/10.1039/c6cy00768f>.
21. Streckova M, Mudra E, Orinakova R, Markusova-Buckova L, Sebek M, Kovalcikova A, et al. Nickel and nickel phosphide nanoparticles embedded in electrospun carbon fibers as favourable electrocatalysts for hydrogen evolution. *Chem Eng J* 2016;303:167e81. <http://dx.doi.org/10.1016/j.cej.2016.05.147>.
22. Jin L, Xia H, Huang Z, Lv C, Wang J, Humphrey MG, et al. Phase separation synthesis of trinickel monophosphide porous hollow nanospheres for efficient hydrogen evolution. *J Mater Chem A* 2016;4:10925e32. <http://dx.doi.org/10.1039/c6ta03028a>.
23. Yan H, Jiao Y, Wu A, Tian C, Zhang X, Wang L, et al. Clusterlike molybdenum phosphide anchored on reduced graphene oxide for efficient hydrogen evolution over a broad PH range. *Chem Commun* 2016;52:9530e3. <http://dx.doi.org/10.1039/c6cc04220a>.
24. Seo B, Baek DS, Sa YJ, Joo SH. Shape effects of nickel phosphide nanocrystals on hydrogen evolution reaction. *CrystEngComm* 2016;18:6083e9. <http://dx.doi.org/10.1039/c6ce00985a>.
25. Yang J, Zhang F, Wang X, He D, Wu G, Yang Q, et al. Porous molybdenum phosphide nanooctahedrons derived from confined phosphorization in UIO-66 for efficient hydrogen evolution. *Angew Chem Int Ed* 2016;55:12854e8. <http://dx.doi.org/10.1002/anie.201604315>.
26. Yang J, Zhang F, Wang X, He D, Wu G, Yang Q, et al. Porous molybdenum phosphide nanooctahedrons derived from confined phosphorization in UIO-66 for efficient hydrogen evolution. *Angew Chem Int Ed* 2016;55:12545e12545. [136] Tian L, Yan X, Chen X. Electrochemical activity of iron phosphide nanoparticles in hydrogen evolution reaction. *ACS Catal* 2016;6:5441e8. <http://dx.doi.org/10.1021/acscatal.6b01515>.
27. Lv C, Yang Q, Huang Q, Huang Z, Xia H, Zhang C. Phosphorus doped single wall carbon nanotubes loaded with nanoparticles of iron phosphide and iron carbide for efficient hydrogen evolution. *J Mater Chem A* 2016;4:13336e43. <http://dx.doi.org/10.1039/c6ta04329a>.
28. Pu Z, Ya X, Amiin IS, Tu Z, Liu X, Li W, et al. Ultrasmall tungsten phosphide nanoparticles embedded in nitrogen doped carbon as a highly active and stable hydrogen evolution electrocatalyst. *J Mater Chem A* 2016;4:15327e32. <http://dx.doi.org/10.1039/c6ta05165k>.
29. Pan Y, Chen Y, Lin Y, Cui P, Sun K, Liu Y, et al. Cobalt nickel phosphide nanoparticles decorated carbon nanotubes as advanced hybrid catalysts for hydrogen evolution. *J Mater Chem A* 2016;4:14675e86. <http://dx.doi.org/10.1039/c6ta06975d>.
30. Zhang X, Han Y, Huang L, Dong S. 3D graphene aerogels decorated with cobalt phosphide nanoparticles as electrocatalysts for the hydrogen evolution reaction. *ChemSusChem* 2016;9:3049e53. <http://dx.doi.org/10.1002/cssc.201600904>.
31. Callejas JF, Read CG, Roske CW, Lewis NS, Schaak RE. Synthesis, characterization, and properties of metal phosphide catalysts for the hydrogen-evolution reaction. *Chem Mater* 2016;28:12798e803. <http://dx.doi.org/10.1021/acs.chemmater.6b02148>.
32. Tian J, Liu Q, Liang Y, Xing Z, Asiri AM, Sun X. FeP nanoparticles film grown on carbon cloth: an ultrahighly active 3D hydrogen evolution cathode in both acidic and neutral solutions. *ACS Appl Mater Interfaces* 2014;6:20579e84. <http://dx.doi.org/10.1021/am5064684>.
33. Zhang X, Meng F, Mao S, Ding Q, Shearer MJ, Faber MS, et al. Amorphous MoS_xCl_y electrocatalyst supported by vertical graphene for efficient electrochemical and photoelectrochemical hydrogen generation.



- Energy Environ Sci 2015;8:862e8. <http://dx.doi.org/10.1039/c4ee03240c>.
34. Zhang H, Yang B, Wu X, Li Z, Lei L, Zhang X. Polymorphic CoSe₂ with mixed orthorhombic and cubic phases for highly efficient hydrogen evolution reaction. ACS Appl Mater Interfaces 2015;7:1772e9. <http://dx.doi.org/10.1021/am507373g>
35. Liu T, Asiri AM, Sun X. Electrodeposited Co-doped NiSe₂ nanoparticles film: a good electrocatalyst for efficient water splitting. Nanoscale 2016;8:3911e5. <http://dx.doi.org/10.1039/c5nr07170d>.
36. Burchardt T. The hydrogen evolution reaction on NiPx alloys. Int J Hydrogen Energy 2000;25:627e34. [http://dx.doi.org/10.1016/S0360-3199\(99\)00089-0](http://dx.doi.org/10.1016/S0360-3199(99)00089-0).
37. Burchardt T. Hydrogen evolution on NiPx alloys: the influence of sorbed hydrogen. Int J Hydrogen Energy 2001;26:1193e8. [http://dx.doi.org/10.1016/S0360-3199\(01\)00053-2](http://dx.doi.org/10.1016/S0360-3199(01)00053-2).
38. Paseka I. Evolution of hydrogen and its sorption on remarkable active amorphous smooth Ni P(x) electrodes. Electrochim Acta 1995;40:1633e40. [http://dx.doi.org/10.1016/0013-4686\(95\)00077-R](http://dx.doi.org/10.1016/0013-4686(95)00077-R).
39. Gao S, Liu Y, Li G, Guo Y, Zou Y, Zou X. General ureaassisted synthesis of carbon-coated metal phosphide nanoparticles for efficient hydrogen evolution electrocatalysis. Electrochim Acta 2016;199:99e107. <http://dx.doi.org/10.1016/j.electacta.2016.03.104>
40. Eftekhari A, Electrocatalysts for hydrogen evolution reaction, International Journal of Hydrogen Energy (2017), <http://dx.doi.org/10.1016/j.ijhydene.2017.02.125>
41. Synthesis, Characterization, and Properties of Metal Phosphide Catalysts for the Hydrogen-Evolution Reaction Juan F. Callejas, Carlos G. Read, Christopher W. Roske, Nathan S. Lewis, and Raymond E. Schaak Chemistry of Materials 2016 28 (17), 6017-6044 DOI: 10.1021/acs.chemmater.6b02148.
42. Pu, Z.; Liu, Q.; Tang, C.; Asiri, A. M.; Sun, X. Ni₂P Nanoparticle Films Supported on a Ti Plate as an Efficient Hydrogen Evolution Cathode. Nanoscale 2014, 6, 11031–11034.
43. Pan, Y.; Hu, W.; Liu, D.; Liu, Y.; Liu, C. Carbon Nanotubes Decorated with Nickel Phosphide Nanoparticles as Efficient Nanohybrid Electrocatalysts for the Hydrogen Evolution Reaction. J. Mater. Chem. A 2015, 3, 13087–13094.
44. Bai, Y.; Zhang, H.; Li, X.; Liu, L.; Xu, H.; Qiu, H.; Wang, Y. Novel Peapod-Like Ni₂P Nanoparticles with Improved Electrochemical Properties for Hydrogen Evolution and Lithium Storage. Nanoscale 2015, 7, 1446–1453.
45. Han, A.; Jin, S.; Chen, H.; Ji, H.; Sun, Z.; Du, P. A Robust Hydrogen Evolution Catalyst Based on Crystalline Nickel Phosphide Nanoflakes on Three-Dimensional Graphene/Nickel Foam: High Performance for Electrocatalytic Hydrogen Production from pH 0–14. J. Mater. Chem. A 2015, 3, 1941–1946.