

Synergistic Nickel phosphide/MXene: An Efficient Hydrogen Evolution Electrocatalyst In Acidic Media

R. SAMAL^{1,†}, C S. ROUT² and P. K. MUKHARJEE^{3,†}

¹*Department of Physics, Chemistry and Biology, Linköping University, Linköping - 58330, Sweden*

²*Centre for Nano and Material Science, Jain University, Bangalore - 562112, India*

³*Experimental Physics VI, Center for Electronic Correlations and Magnetism, Institute of Physics, University of Augsburg, Augsburg-86159, Germany*

†E mail: samalrutuparna@gmail.com , pkmukharjee92@gmail.com

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Abstract. Electrocatalysis plays a crucial role in the development of sustainable approaches for generating hydrogen as a clean energy source. Hydrogen is considered a promising and clean fuel for various applications, including energy storage and transportation. Developing effective and affordable electrocatalysts is crucial to make water splitting economically viable and environmentally sustainable. Herein, we have taken a commendable step towards understanding the synergistic correlation of metal phosphide (Ni₂P) and MXene (Ti₃C₂T_x) hybrid structures for efficient catalyst for hydrogen evolution. The Ni₂P/Ti₃C₂T_x hybrid structure outperformed from its bare phosphide counter part with an overpotential (@ 10 mA/cm²) of 351 mV, tafel slope of 95 mV/dec with excellent stability profile sustaining up to 11000 secs. This work further provides new pathways to dig up on other phosphide and MXene structures towards sustainable and low cost electrocatalyst.

Keywords: Hydrogen evolution, electrocatalyst, MXene, Tafel slope

1. Introduction

Electrolysis of water is a key method for producing hydrogen, and efficient electrocatalysts are essential for this process. Electrocatalysts facilitate these reactions by lowering the activation energy, making the process more energy-efficient. The most common electrocatalysts for hydrogen [1] evolution reactions are based on precious metals like platinum, but these materials are expensive and scarce, limiting their large-scale application. Researchers are actively working on the design and optimization of catalysts made from abundant and less expensive

materials. Some promising materials include metal oxides[2], metal sulphides[3], phosphides[4], carbon-based materials[5], and various hybrid structures[6].

In this work, the goal is to enhance the catalytic activity, stability, and selectivity of these materials to improve the overall efficiency of hydrogen evolution. Additionally, we have explored hybrid structures of Ti based MXene with Nickel phosphide and tuned the electronic properties of the electrocatalyst in the acidic electrolyte environment. This communication delves into physicochemical properties comparison between pure Nickel phosphide (Ni_2P) and its hybrid material.

2. Experimental

The synthesis of pristine $\text{Ti}_3\text{C}_2\text{T}_x$ stacked sheets involved the use of MAX phase obtained from Carbon-Ukraine. Initially, the MAX phased powder was added gradually to the etching process, selectively removing the aluminium layer with concentrated HF solvent. This etching details can be found elsewhere [7].

The pristine transition metal tellurides were synthesized using a conventional hydrothermal approach. In this method, 40 mL of distilled water was employed as the solvent, and cobalt/nickel nitrate precursors ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\geq 99.9\%$ from Merck, were added to the solution. The mixture underwent stirring for 20 minutes, after which well dispersed Red phosphorous and MXene solution was added and pH of the mixture was maintained to ~ 13 . Following that, the dark maroon solution was moved to a 100 mL autoclave and heated at 180°C for a duration of 18 hours, afterwards it was allowed to cool down naturally to room temperature. The ultimate product was then collected, subjected to repeated washing with both distilled water and ethanol, and subsequently dried at 70°C .

3. Results and discussion

Ni_2P crystallizes in the hexagonal crystal structure with space group P-62m (SG no. 189). The crystal structure comprises two Ni and P sites. Distorted honeycomb-like structures are formed by the Ni1, P1, and P2 sites spread in the ab-plane, with the Ni2 site consistently positioned at the center of the honeycomb. Furthermore, the honeycomb patterns connect along the c-direction via P2 sites. **Figure 1 (a)** depicts the crystal structure of Ni_2P featuring honeycomb like patterns. VESTA software was used for crystal structure visualization of the same. **Figure 1 (b)** illustrates the powder XRD pattern taken at room temperature. Profile fitting (Le-Bail) of the XRD data was conducted using the FULLPROF software package [8]. All the observed peaks align well with the theoretical patterns of Ni_2P . Subsequently, the peaks were successfully

fitted using the pseudo-Voigt function. The best fit was achieved with the following lattice parameters: $a = b = 5.8675 (2) \text{ \AA}$, $V_{\text{cell}} = 101.093(1) \text{ \AA}^3$. These obtained lattice parameters align well with the previous report [9]. Nevertheless, the presence of the 002 plane in **Figure 1 (c)** with green line, signifies the successful incorporation of the layered $\text{Ti}_3\text{C}_2\text{T}_x$ structure, as indicated by the peak at 2θ , maintaining an approximate value of $\sim 9^\circ$ degrees. The diffractograms of the pure and the hybrid with MXene exhibit similar XRD pattern because of the low concentration of MXene incorporation.

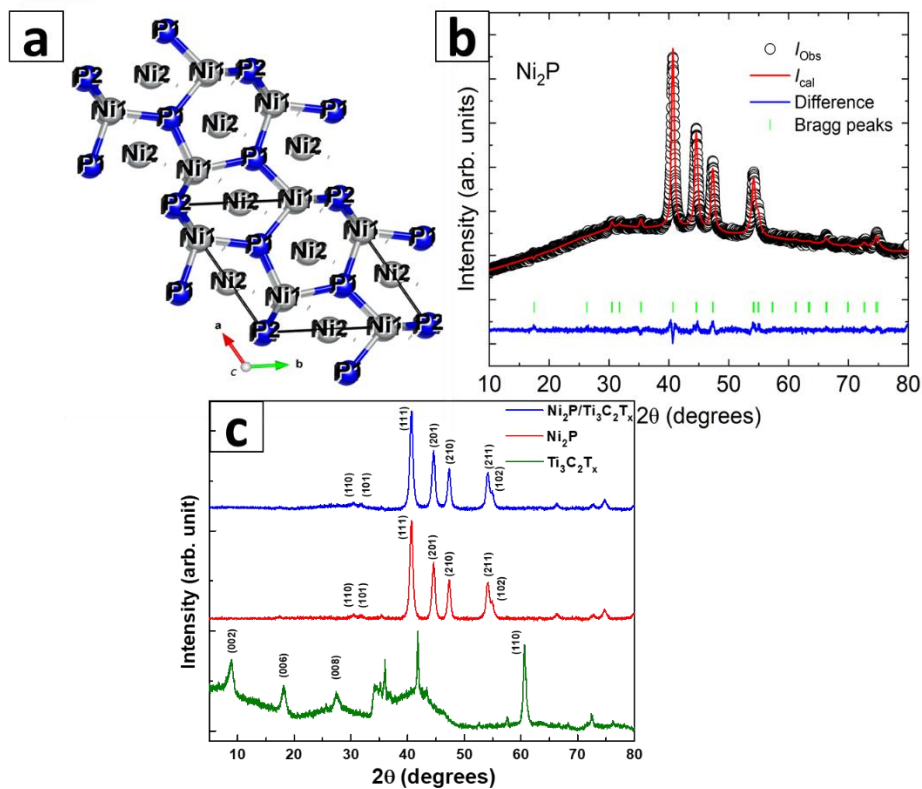


Fig. 1: (a) Crystal Structure of honeycomb Ni_2P , Powder x-ray diffraction of Ni_2P with (b) Le-Bail fitting (The solid red line shows the profile fit of the data. The green vertical lines show the Bragg positions. The bottom blue line depicts the difference between the experimentally obtained and the calculated XRD intensities), (c) merged diffractograms of as-prepared samples collected at room temperature.

In **Figure 2**, scanning electron microscopy images illustrate the morphology of as-received hydrothermally synthesized nickel phosphide powder. The as-received Ni_2P exhibits a variety of shapes, with an average crystalline size ranging around ~ 10 microns. Notably, it displays a distinctively rough surface morphology [**Figure 2 (c)**]. Further, the **Figure 2 (d)** elucidates the stacked MXene layers decorated with the rough Ni_2P particulate nanostructures proving the presence of both components.

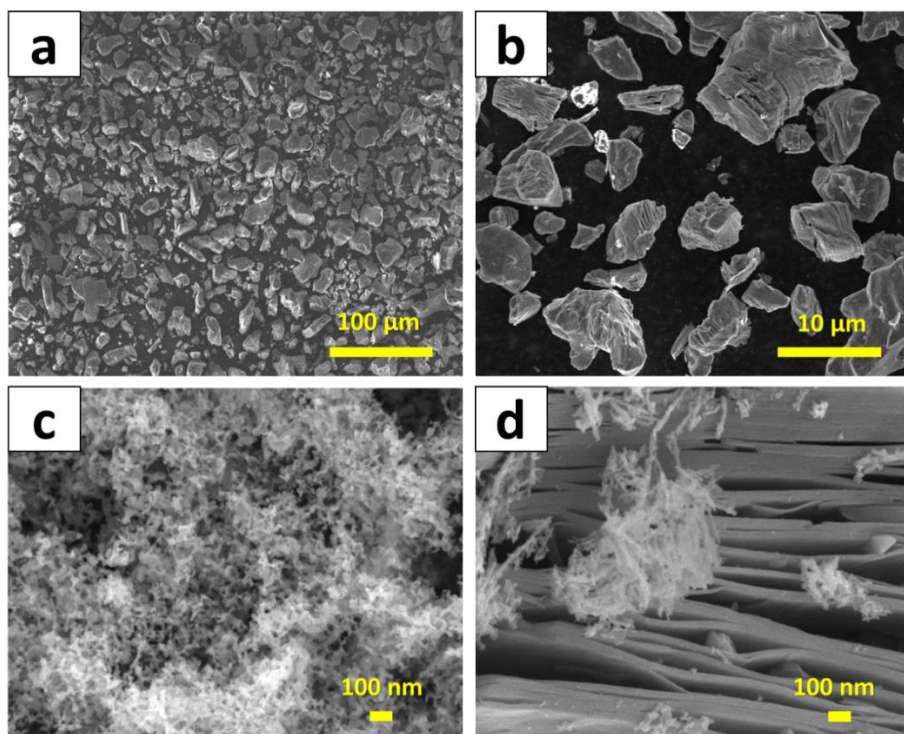


Fig. 2: Scanning electron micrographs of (a) MAX, (b) $\text{Ti}_3\text{C}_2\text{T}_x$, (c) Ni_2P , (d) $\text{Ni}_2\text{P}/\text{Ti}_3\text{C}_2\text{T}_x$.

In a three-electrode system, we conducted tests on the hydrogen evolution reaction (HER) catalytic activities of various catalysts in a 0.5 M H_2SO_4 solution. **Figure 3 (a)** depicts the HER polarization curves for the hybrid structures of Ni_2P , $\text{Ni}_2\text{P}/\text{Ti}_3\text{C}_2\text{T}_x$, standard commercial platinum carbon (Pt/C) and glassy carbon (GC) substrate.

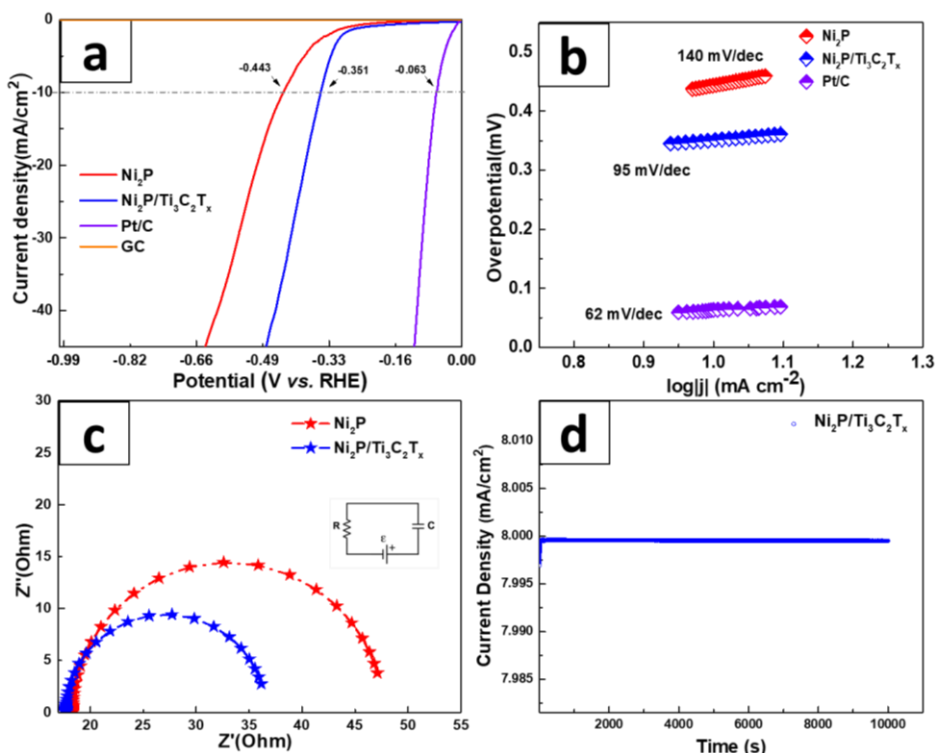


Fig. 3:(a) Linear sweep voltametric diagrams, (b) Tafel slope, (c) electrochemical impedance spectroscopy of the standard and as-prepared samples, (d) Stability of the hybrid Ni₂P/Ti₃C₂T_x.

At a current density of 10 mA cm⁻², the overpotential of Pt/C, pure and Ni₂P/Ti₃C₂T_x hybrid structure were recorded to be 63 mV, 443 mV, 351 mV respectively. Notably, among the two as-synthesized catalysts, Ni₂P/Ti₃C₂T_x exhibited the lowest overpotential. The HER kinetics of the electrocatalysts were investigated using Tafel plots [10]. In **Figure 3 (b)** the Tafel slopes were calculated to be 140, 95 and 62 mV per decade for Ni₂P, Ni₂P/Ti₃C₂T_x, and Pt/C, respectively. In the absence of MXene support, sample exhibit Tafel slope values surpassing those of the corresponding hybrids. To gain deeper insights into the superior hydrogen evolution reaction activity of the Ni₂P/Ti₃C₂T_x MXene hybrid, electrochemical impedance spectroscopy (EIS) was conducted on the as-prepared catalysts. The Nyquist plots, featuring equivalent Randles circuits for the electrodes, are presented in **Figure 3 (c) inset**. Notably, the charge transfer resistance (R) of the hybrid sample is recorded at 29 Ω, the smallest among the tested electrocatalysts. This indicates that the synergistic effect plays a crucial role in tuning the intrinsic catalytic activity. For a comprehensive assessment of long-term stability, time-dependent chronoamperometric response (i-t)

measurements of the hybrid catalyst under optimized conditions reveal that the current density of the Ni₂P/Ti₃C₂T_x MXene hybrid remains well-maintained without significant amplification for over 11000 secs (**Figure 3 (d)**). This further validates its exceptional durability.

4. Conclusion

The MXene based hybrid samples were prepared by a naive one step hydrothermal route. Remarkably, the Ni₂P/Ti₃C₂T_x hexagonal hybrid system showcases the most superior catalytic performance in the HER, as it displays the smallest overpotential, excellent stability and Tafel slope among the tested samples. This research offers an innovative approach for designing and fabricating composite materials using single/bimetal phosphides and Ti₃C₂T_x. It holds great promise to create electrocatalysts with enhanced efficiency for addressing the challenges associated with sustainable hydrogen production but also have broader implications for other electrochemical processes, such as fuel cells and various energy storage technologies.

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References

- [1] M. S. Dresselhaus, and I. L. Thomas. *Nature* **414**, 6861 (2001).
- [2] Y. Zhu, Q. Lin, Y. Zhong, H. A. Tahini, Z. Shao, and H. Wang. *Energy Environ. Sci.* **13**,10 (2020).
- [3] H. G. Shiraz, X. Crispin, and M. Berggren. *Int. J. Hydrog. Energy* **46**, 47 (2021).
- [4] P. Xiao, W. Chen, and X. Wang. *Adv. Energy Mater.* **5**, 24 (2015).
- [5] W. Zhou, J. Jin, J. Lu, L. Yang, D. Hou, G. Li, and S. Chen. *Nano Energy* **28**, 29 (2016).
- [6] Q. Hu, L. Guomin, Z. Han, Z. Wang, X. Huang, H. Yang, Q. Zhang, J. Liu, and C. He. *J. Mater. Chem. A* **7**, 24 (2019).
- [7] R. Samal, C. Debbarma, and C. S. Rout. *Catal. Today* **424**, 113880 (2023).
- [8] J. Rodríguez-Carvajal, *Phys. B: Condens. Matter* **192**, 55 (1993).
- [9] H. N. Nowotheny, E. Henglein, *Zeitschrift für Phys. Chemie* **40**, 281 (1938).
- [10] B. V Tilak, and C. P Chen. *J. Appl. Electrochem.* **23**, 6 (1993).