

Phase Transformations in the Nickel Phosphide System Induced by Transition-Metal Doping and Electrocatalytic Study

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Introduction



Figure 1. Electrochemical reactions and applications of nickel phosphides.

- Functional nanomaterials such as nickel phosphides (NiP) are desired today as catalysts in energy generation and storage.
- Phase transformations within the NiP system is rare and can be explored to improve catalyst performance.

Formation of nickel phosphides.

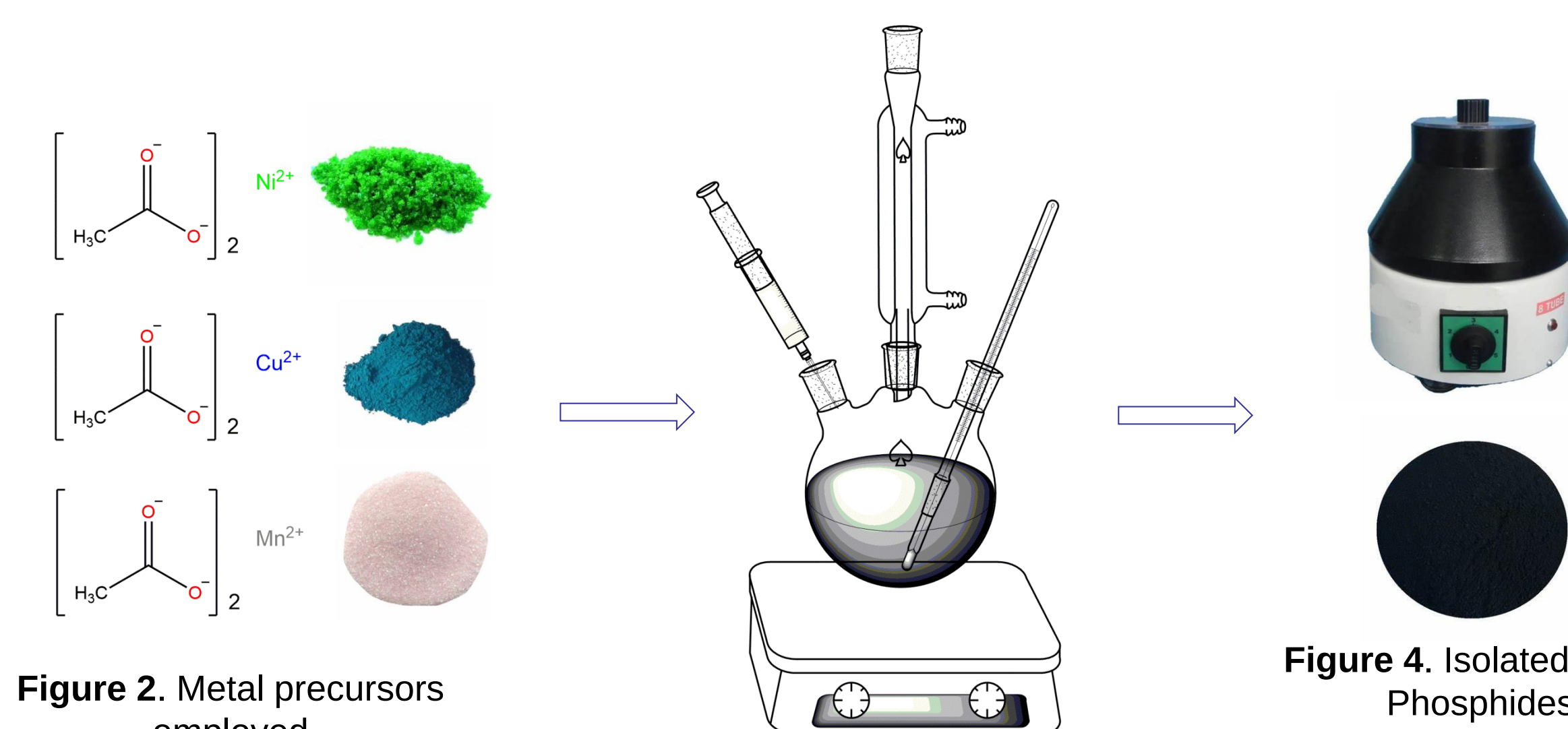


Figure 2. Metal precursors employed

Figure 3. Hot injection setup for NiP formation and transformation

Figure 4. Isolated Nickel Phosphides

PXRD Characterization

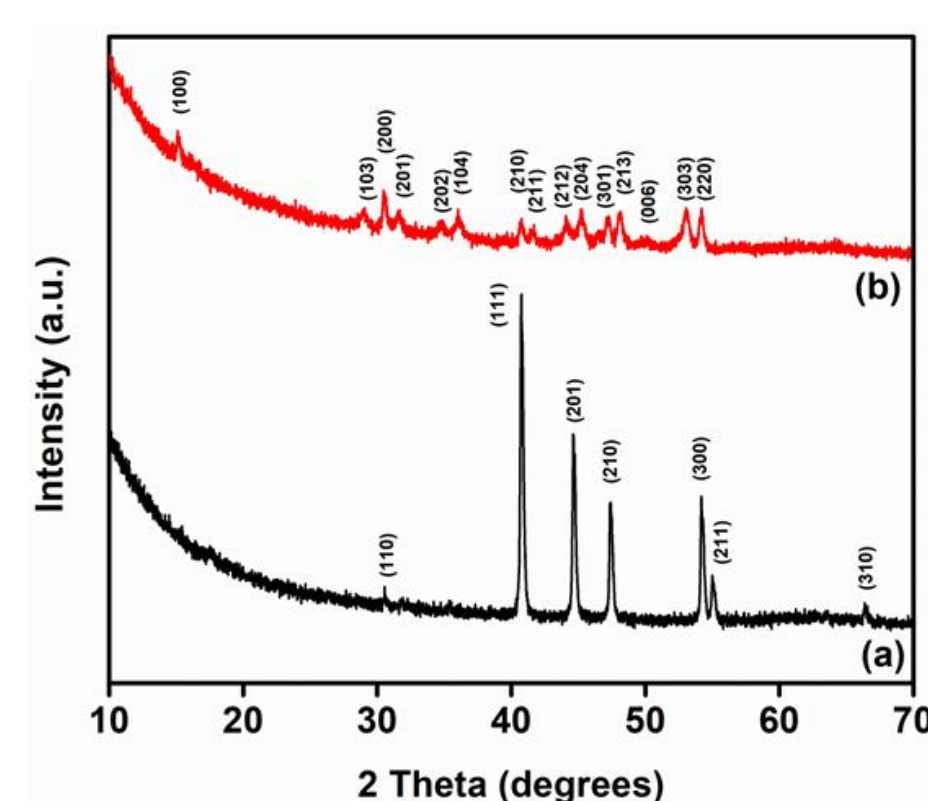


Figure 5. Powder-XRD patterns of the decomposition of Ni(Ac)₂.4H₂O in (a) TOPO/TOP and (b) HDA/TOP at 300 °C for 1 hr.

- Hexagonal Ni₂P were formed on decomposition of Nickel acetate in TOPO/TOP.
- On the other hand, decomposition in HDA/TOP Yielded hexagonal Ni₅P₄.



We demonstrated chameleonic phase transformations of formed phosphides by doping.

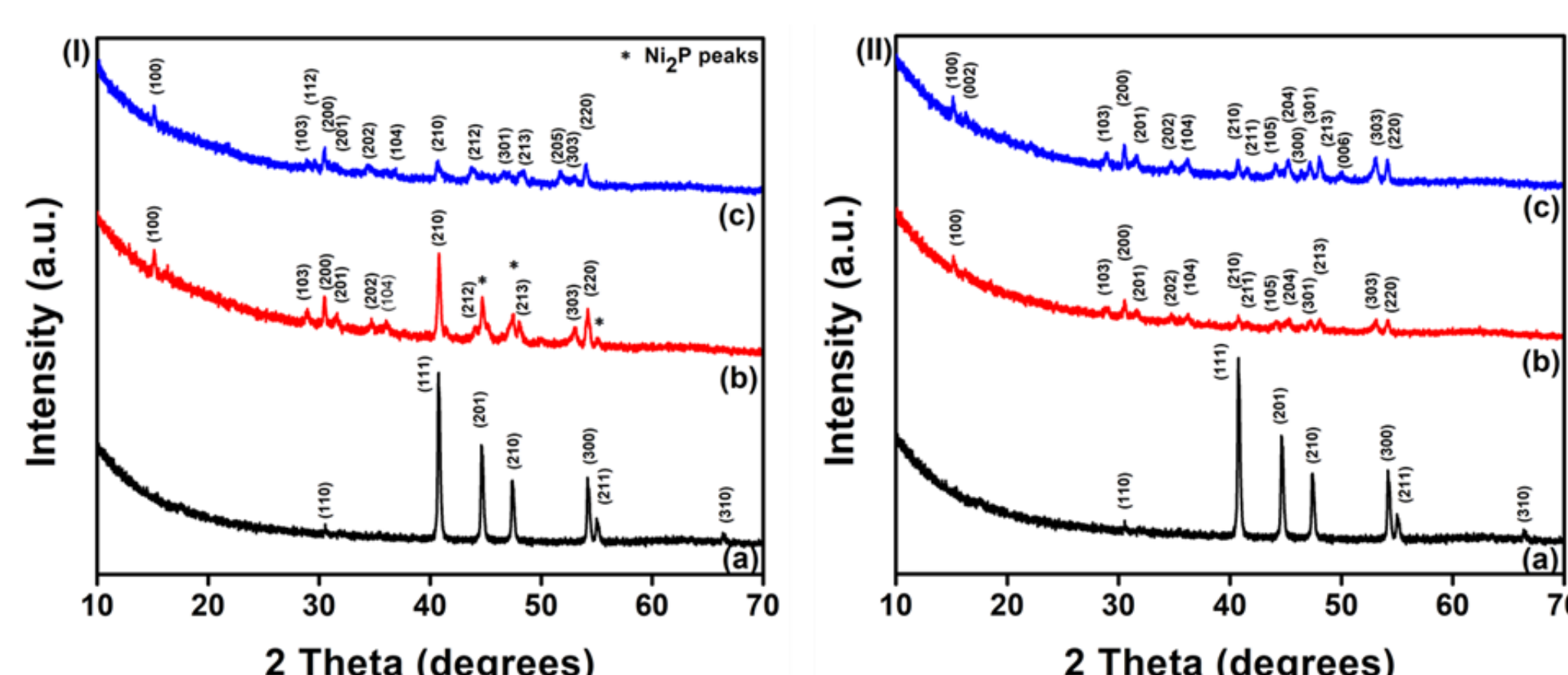


Figure 6. (I) Patterns of (a) the decomposition of Ni(Ac)₂.4H₂O in TOPO/TOP [Ni₂P], (b) 5% and (c) 10% Cu doped Ni₂P yielding Ni₅P₄. (II) Patterns of (a) the decomposition of Ni(Ac)₂.4H₂O in TOPO/TOP [Ni₂P], (b) 5% and (c) 10% Mn doped Ni₂P forming Ni₅P₄.

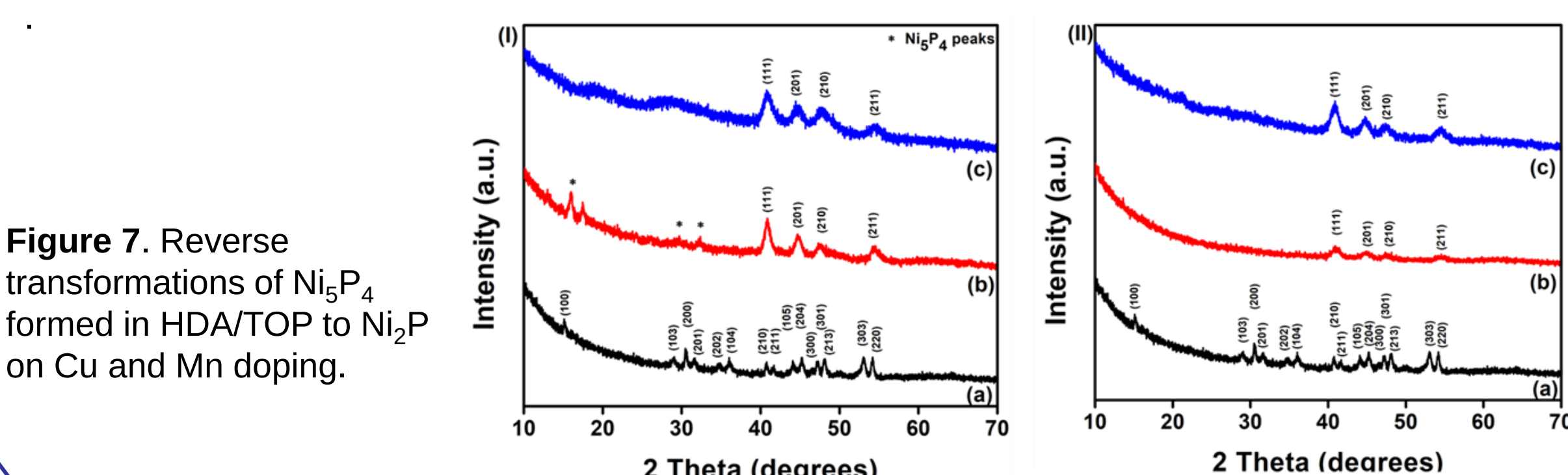


Figure 7. Reverse transformations of Ni₅P₄ formed in HDA/TOP to Ni₂P on Cu and Mn doping.

Structure analysis

Table 1. Summary of formed and transformed nickel phosphides.

Nickel precursor	Solvents	Dopants	Formed phase
Ni(Ac) ₂ .4H ₂ O	TOPO/TOP	–	NiP-1 (Ni ₂ P)
Ni(Ac) ₂ .4H ₂ O	TOPO/TOP	5% Cu	Ni ₅ P ₄ + Ni ₂ P
Ni(Ac) ₂ .4H ₂ O	TOPO/TOP	10% Cu	NiP-3 (Ni ₅ P ₄)
Ni(Ac) ₂ .4H ₂ O	TOPO/TOP	5% Mn	Ni ₅ P ₄
Ni(Ac) ₂ .4H ₂ O	TOPO/TOP	10% Mn	NiP-4 (Ni ₅ P ₄)
Ni(Ac) ₂ .4H ₂ O	HDA/TOP	–	NiP-2 (Ni ₅ P ₄)
Ni(Ac) ₂ .4H ₂ O	HDA/TOP	5% Cu	Ni ₂ P + Ni ₅ P ₄
Ni(Ac) ₂ .4H ₂ O	HDA/TOP	10% Cu	NiP-5 (Ni ₂ P)
Ni(Ac) ₂ .4H ₂ O	HDA/TOP	5% Mn	Ni ₂ P
Ni(Ac) ₂ .4H ₂ O	HDA/TOP	10% Mn	NiP-6 (Ni ₂ P)

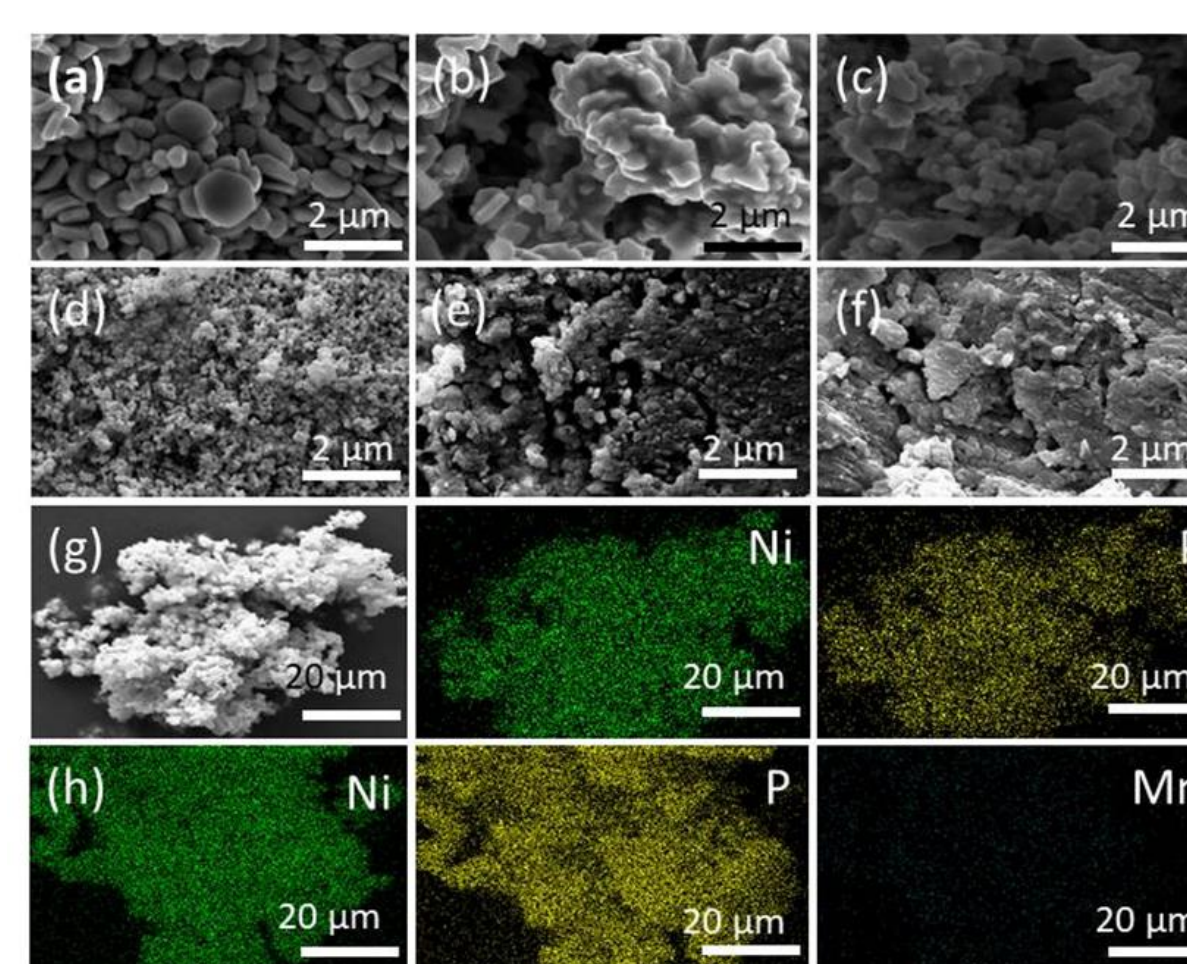


Figure 8. SEM images of (a) NiP-1, (b) NiP-3 (c) NiP-4 (d) NiP-2 (e) NiP-5 and (f) NiP-6. Representative EDX elemental mapping images of (g) NiP-1 and (h) NiP-2.

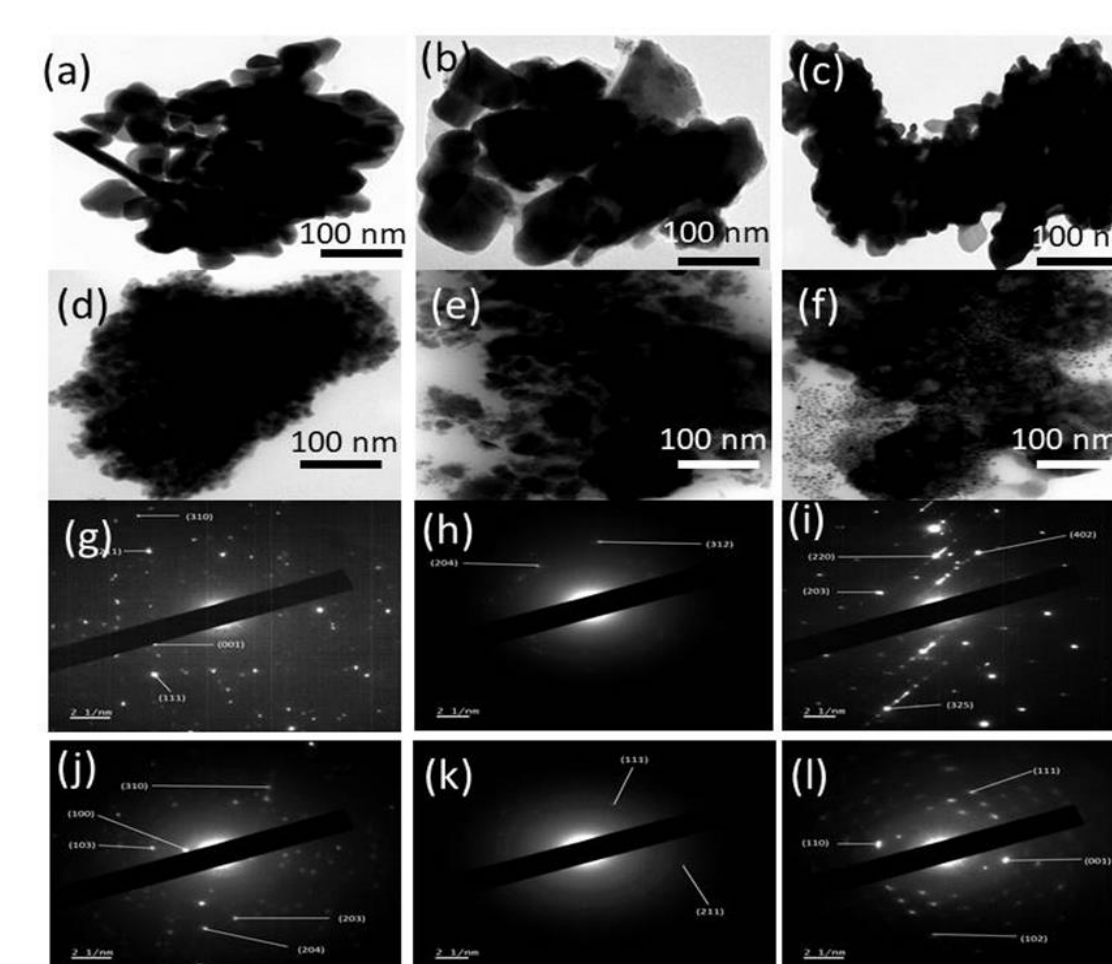


Figure 9. TEM images of (a) NiP-1, (b) NiP-3 (c) NiP-4 (d) NiP-2 (e) NiP-5 and (f) NiP-6. SAED images of (g) NiP-1, (h) NiP-3 (i) NiP-4 (j) NiP-2 (k) NiP-5 and (l) NiP-6.

Electrocatalytic properties

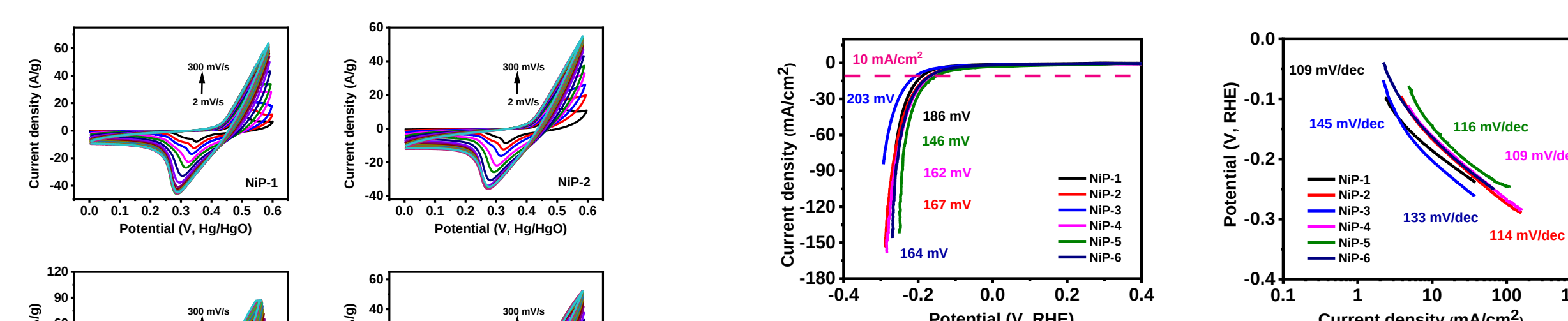


Figure 10. CV curves of NiP electrodes

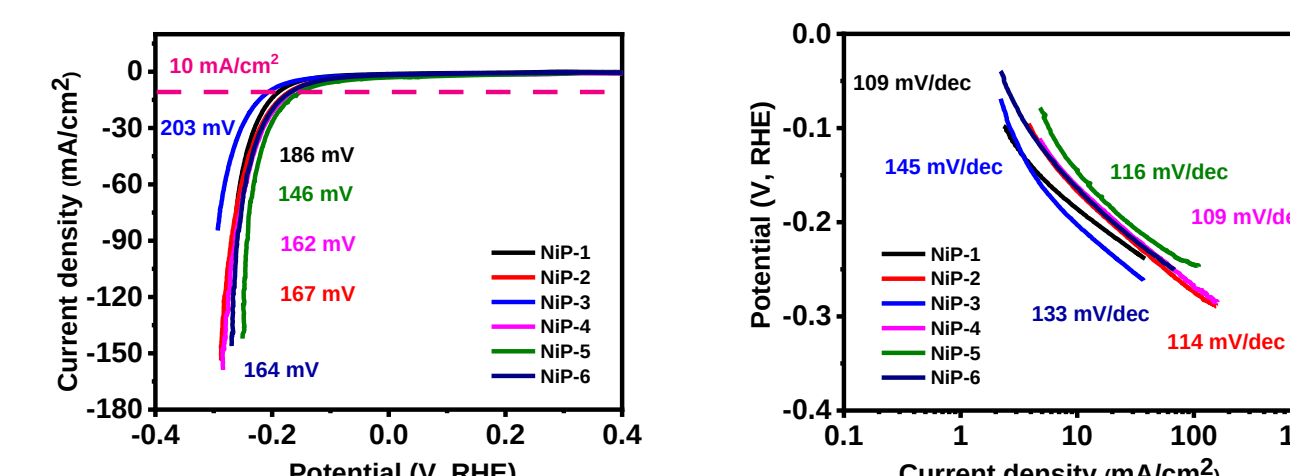


Figure 11. HER performance of NiP electrodes in terms of overpotential and Tafel slope.

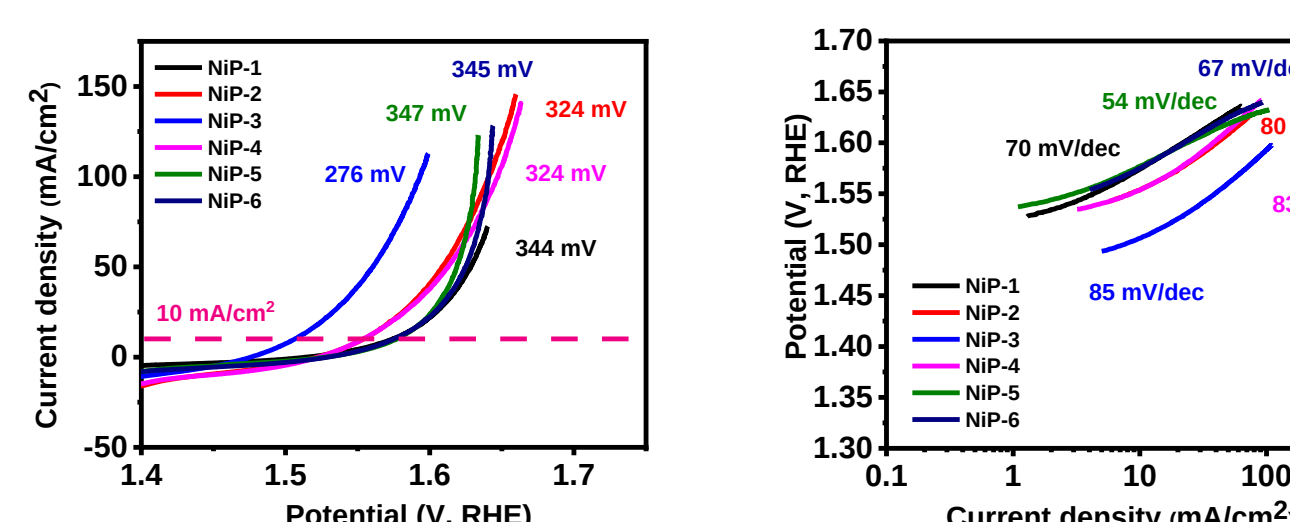


Figure 12. OER performance of NiP electrodes in terms of overpotential and Tafel slope.

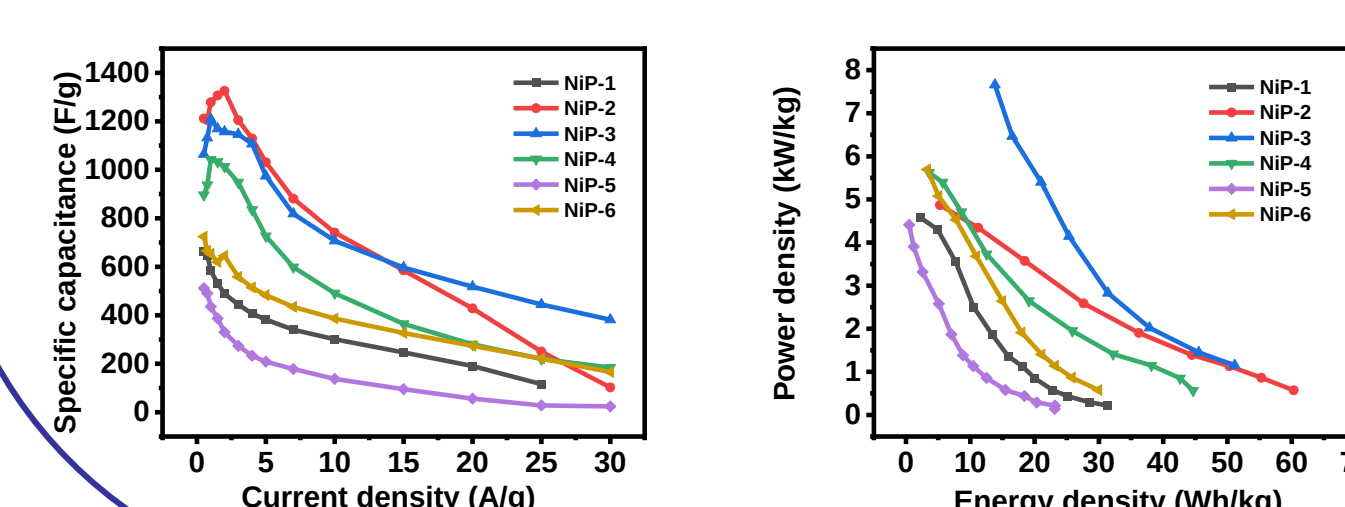


Figure 13. Variation of specific capacitance as a function of current density and (b) Ragone plots for the NiP samples.

Conclusion

- Ni₂P and Ni₅P₄ were formed in TOPO/TOP and HDA/TOP, respectively.
- Ni₂P was transformed to Ni₅P₄ on doping with Cu and Mn in TOPO/TOP
- The reverse transformation from Ni₅P₄ to Ni₂P was observed in HDA/TOP
- Formed and transformed phosphides showed good overall water splitting catalytic performance

Acknowledgement

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