Facile and environmentally friendly synthesis of transition metal phosphides based nanocomposite electrocatalysts for hydrogen evolution from water

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Transition metal phosphides and their nanocomposites are considered to be one of the most promising Pt-free hydrogen evolution reaction (**HER**) electrocatalysts. At the same time, obtaining of nanocomposite electrocatalysts based on d-metal phosphides is often a complex and multi-stage process, and also requires the use of environmentally hazardous phosphorus compounds.

We have proposed a universal approach to obtaining nanocomposite electrocatalysts for hydrogen evolution from water based on d-metal phosphides (**Co, Ni, Mo, Fe, V**) and N,P-doped carbon. The approach involves the pyrolysis (at 900ºC in an inert atmosphere) of H_3PO_4-doped polyaniline together with the salt of the corresponding metal. The proposed approach has advantages such as the simplicity of its implementation, the low cost of the initial reagents and the absence of toxic compounds among them.

The formation of phosphides in the obtained composites has been confirmed by X-ray phase analysis, regardless of the type of d-metal (except for vanadium, where nitride phosphide was formed) (**Fig.1**). It has been found that **FeP**, **MoP**, and $\mathbf{V_5NP_3}$ are the sole metal-rich crystalline phases in their respective hybrid materials. However, in the case of **Co**- and **Ni**-containing composites, a coexistence of two phases is observed ($\mathbf{Co_2P}$ as the dominant phase along with **CoP**; $\mathbf{Ni_2P}$ as the dominant phase along with $\mathbf{Ni_{12}P_5}$).

The ability of all the obtained nanocomposites to exhibit electrocatalytic activity in the HER has been determined in 0.5 M H_2SO_4 and 1.0 M NaOH aqueous solutions (**Fig. 2**). However, the type of phosphides in the composite materials, which serve as the main active sites in HER, significantly influences the efficiency of electrochemical hydrogen evolution from water. It has been demonstrated that the most effective electrocatalyst in acidic electrolyte is based on Ni_xP_y (with a Tafel slope, b~60 mV/dec and an overpotential at 10 mA/cm^2, η_{10}~150 mV), while in alkaline electrolyte, the catalyst based on MoP shows the highest efficiency (b~84 mV/dec and η_{10}~126 mV) (**Table**). Based on the determined b values (55-112 mV/dec) for the synthesized catalysts, it can be suggested that the hydrogen evolution proceeds via the Volmer-Tafel mechanism.

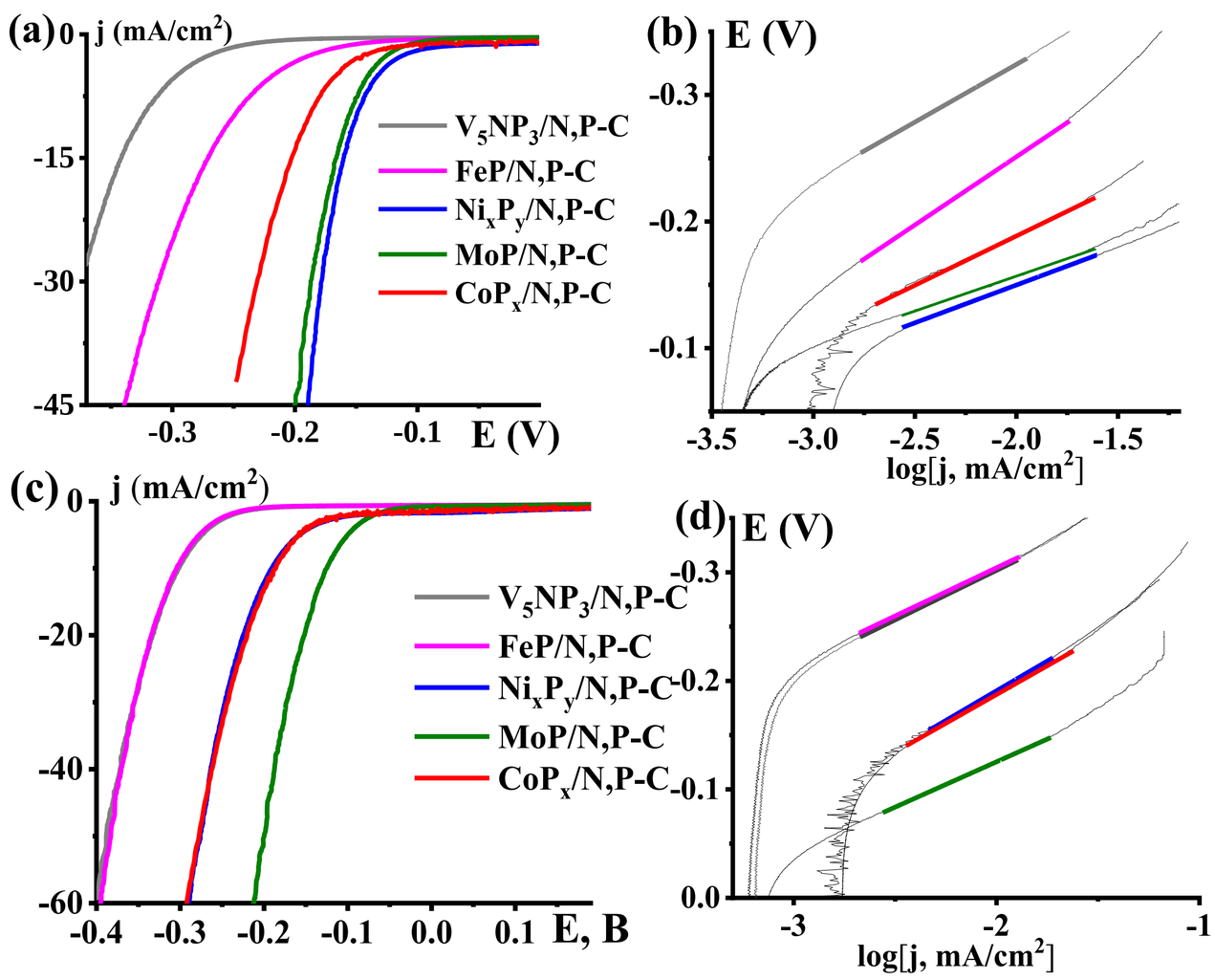

Fig. 2. The HER polarization curves (a, c) and Tafel slopes (b, d) for obtained composites in 0.5 M H_2SO_4 (a, b) and 1.0 M NaOH (c, d)

Fig.1. XRD pattern of obtained composites

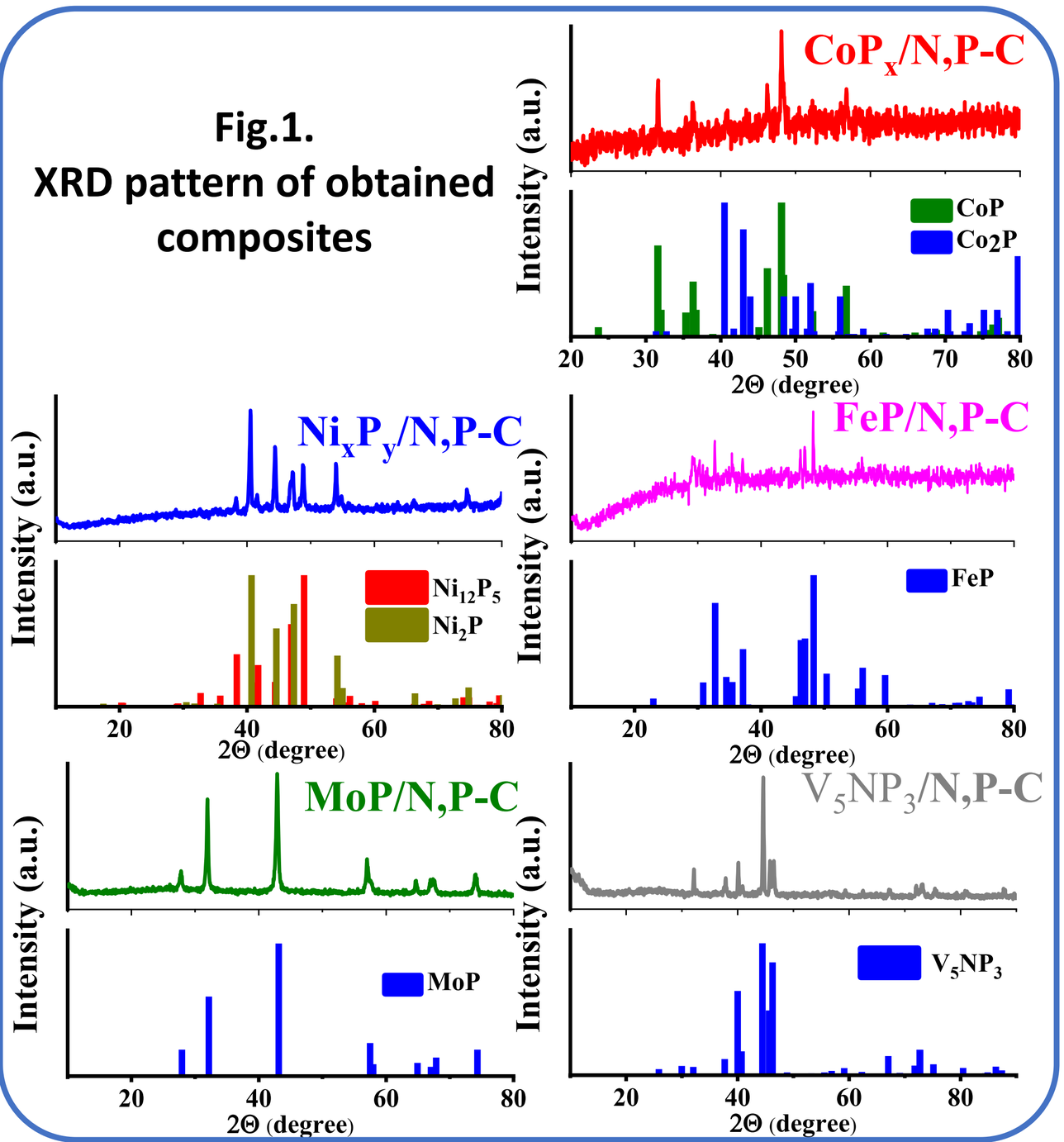

TABLE. HER PERFORMANCE OF ELECTROCATALYSTS

Electrocatalysts	Electrolyte	*b*, mV/dec	η_{10}, mV
Ni_xP_y/N,P-C	0.5M H_2SO_4	60	150
MoP/N,P-C		55	157
CoP_x/N,P-C		74	189
FeP/N,P-C		108	250
V_5NP_3/N,P-C		91	325
Ni_xP_y/N,P-C	1.0M NaOH	109	190
MoP/N,P-C		84	126
CoP_x/N,P-C		112	187
FeP/N,P-C		89	305
V_5NP_3/N,P-C		91	304