Photovoltaic-powered electrocatalytic water splitting is a promising method for realizing a sustainable energy system based on H₂ fuel.¹ In this regard, both hydrogen evolution catalysts and oxygen evolution catalysts play key roles in determining the efficiency of water splitting reaction. For the hydrogen evolution reaction (HER), platinum (Pt) is the most efficient catalyst, but its rarity on Earth crust and thus high costs prevent large-scale implementation.² Substantial research effort is currently being directed toward developing efficient and stable catalysts from earth-abundant materials using low-cost synthesis methods.

Metal phosphides, which are well-known active catalysts for hydrodesulfurization,³ have been recently revealed to be also active catalysts for HER.⁴⁻⁸ Given their high activity and stability during operation, metal phosphides have emerged as promising earth-abundant alternative to Pt for electrocatalytic HER. To outperform Pt, the HER activities of existing monometallic phosphides (e.g., Ni₂P, CoP, FeP, and MoP) need to be improved. Previous studies show that modifying the electronic properties using cationic substitution to form bimetallic phosphides leads to superior activity as compared to the parent monometallic phosphides.⁹⁻¹³

In an effort to expand the bimetallic phosphide family, we report a simple and scalable synthesis of nickel-iron phosphide films, with precisely controlled metal content, on Ti foils using a two-step strategy of spray-pyrolysis deposition followed by low-temperature phosphidation. The direct deposition of these films on Ti foils to form electrodes has not only omitted the use of binders, but has also minimized the electrical resistance previously caused by poor connection between the catalyst and the current collector, making this method more advantageous as compared to powder-derived electrodes.

The nickel-iron phosphide of an optimized Ni:Fe ratio of 1:4 demonstrated remarkable overall catalytic activity for HER in 0.5 M H₂SO₄ as compared to nickel phosphide and iron phosphide, achieving current densities of -10 mA cm⁻² and -30 mA cm⁻² at overpotentials of 101 mV and 123 mV, respectively, with a Tafel slope of 43 mV dec⁻¹ (see Figure 1). It also showed a near-100% Faradaic efficiency and an excellent catalytic stability. The superior overall HER activity of nickel-iron phosphide relative to nickel phosphide and iron phosphide is a combined contribution from the larger real surface area (thus a higher number of reaction sites for HER) and the higher intrinsic catalytic activity for HER. The latter was revealed by X-ray photoelectron spectroscopy analysis to be a result of a decreased partial positive charge at Fe sites and an increased partial negative charge at P sites, which make the Fe and P sites better hydride- and proton acceptors, respectively. The two-step synthesis method reported herein offers a convenient approach for exploring multi-transition metal phosphides for expanding the library of low-cost and efficient catalysts.
Figure 1. (Left) SEM image of the surface morphology of nickel-iron phosphide film (Ni:Fe 1:4). (Middle) Polarization curve for HER measured in 0.5 M H₂SO₄. Inset shows the change in overpotential during a 24-h stability test at -10 mA cm⁻². (Right) Faradaic efficiency measurement.

References