

A Nickel-Iron Diselenide-Derived Efficient Oxygen Evolution Catalyst

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The (OER) is the bottleneck in water splitting. The development of efficient, abundant, and inexpensive oxygen evolution reaction (OER) catalysts is one of the main themes of current research in renewable energies.¹ Recently, a few non-oxide-based OER catalysts including metal phosphides, sulfides, and selenides are reported.² Given the limited stability of these compounds under highly oxidative potentials

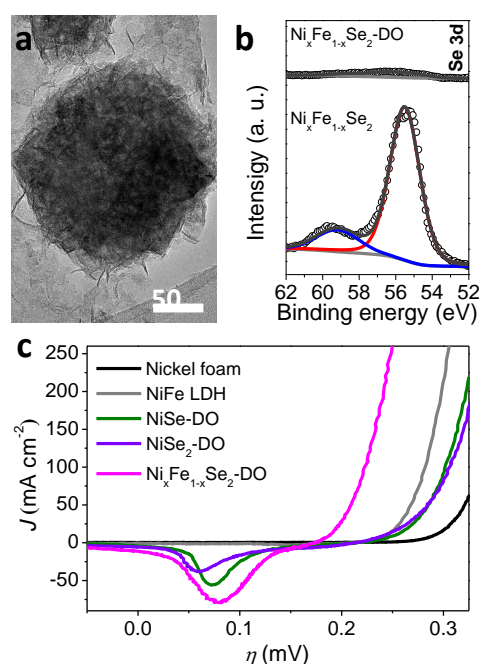


Fig. 1 (a) TEM image of $\text{Ni}_x\text{Fe}_{1-x}\text{Se}_2\text{-DO}$. (b) High resolution XPS spectra of Se 3d of $\text{Ni}_x\text{Fe}_{1-x}\text{Se}_2\text{-DO}$ and $\text{Ni}_x\text{Fe}_{1-x}\text{Se}_2$. Se almost disappeared in $\text{Ni}_x\text{Fe}_{1-x}\text{Se}_2\text{-DO}$. (c) Polarization curves of $\text{Ni}_x\text{Fe}_{1-x}\text{Se}_2\text{-DO}$, NiFe LDH, NiSe₂-DO,

in alkaline solutions, questions have arisen on the nature of the true active species. Indeed, we and others showed that the surfaces of Ni₂P and CoP were transformed into metal oxides during catalysis, which were responsible for the catalytic activity.^{2a,e} For Ni, Co and Fe sulfides, Cui and co-workers showed that they were entirely transformed into the corresponding metal oxides during OER.^{2b} Since metal selenides have similar chemical reactivity to metal sulfides, we were surprised by previous reports which suggested stability of bulk NiSe, Ni₃Se₂, and CoSe₂ materials under OER.^{2c,d}

Using a post-catalytic analysis, we show here that NiSe is completely converted into nickel hydroxides during OER, indicating that metal oxides or hydroxides are the active and final forms of metal selenides pre-catalysts in OER. This knowledge promoted us to purposely use metal selenides as templating precursors to highly active metal oxide OER catalysts, because methods to produce ultrasmall nanostructured metal selenides are readily available. Following this strategy, we synthesized a hitherto unknown selenide, nickel iron diselenide ($\text{Ni}_x\text{Fe}_{1-x}\text{Se}_2$), which upon in-situ transformation into oxides (Fig. 1a and 1b), catalyzes OER with an overpotential of only 195 mV for a current density of 10 mA cm⁻² (Fig. 1c). This is until now the most active single-phase OER catalyst in alkaline solutions. The high activity of this $\text{Ni}_x\text{Fe}_{1-x}\text{Se}_2$ -derived oxides ($\text{Ni}_x\text{Fe}_{1-x}\text{Se}_2\text{-DO}$) is largely due

to its desirable nanostructure (Fig. 1a), inherited from its selenide precursor. Our work underscores the importance to identify the active species of OER catalysts, and demonstrates how such knowledge can be applied to develop better catalytic materials. The templating approach described here might be applicable for the synthesis of other metal oxide-based nanomaterials.

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