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# Enhancing Oxygen Evolution Reaction Performance in Prussian Blue Analogues: Triple-Play of Metal Exsolution, Hollow Interiors, and Anionic Regulation

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Prussian blue analogs (PBAs) are promising catalysts for green hydrogen production. However, the rational design of high-performing PBAs is challenging, which requires an in-depth understanding of the catalytic mechanism. Here FeMn@CoNi core-shell PBAs are employed as precursors, together with Se powders, in low-temperature pyrolysis in an argon atmosphere. This synthesis method enables the partial dissociation of inner FeMn PBAs that results in hollow interiors, Ni nanoparticles (NPs) exsolution to the surface, and Se incorporation onto the PBA shell. The resulting material presents ultralow oxygen evolution reaction (OER) overpotential (184 mV at 10 mA cm<sup>-2</sup>) and low Tafel slope (43.4 mV dec<sup>-1</sup>), outperforming leading-edge PBA-based electrocatalysts. The mechanism responsible for such a high OER activity is revealed, assisted by density functional theory (DFT) calculations and the surface examination before and after the OER process. The exsolved Ni NPs are found to help turn the PBAs into Se-doped core-shell metal oxyhydroxides during the OER, in which the heterojunction with Ni and the Se incorporation are combined to improve the OER kinetics. This work shows that efficient OER catalysts could be developed by using a novel synthesis method backed up by a sound understanding and control of the catalytic pathway.

# 1. Introduction

The depletion of traditional energy sources and their environmental impacts have motivated researchers to vigorously pursue alternative energy solutions.<sup>[1,2]</sup> Among them, green hydrogen has emerged as a promising candidate due to its high gravimetric energy density and net-zero emission.[3,4] Electrochemical water splitting, powered by renewable energy, is highly desirable to produce green hydrogen at a large scale.<sup>[5]</sup> However, the efficiency of this process is hindered by intrinsically sluggish kinetics involving multiple proton-coupled electron transfers in the oxygen evolution reaction (OER), which demands a large overpotential and the use of expensive and scarce materials as the catalyst.<sup>[6,7]</sup> Thus, the search is still ongoing for highly cost-effective OER electrocatalysts.

Prussian blue analogs (PBAs), one type of metal–organic framework, have shown potential in catalyzing the splitting of

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waterdue to their size uniformity, high porosity, tunable morphologies, and variable compositions.<sup>[8–10]</sup> The control over their morphology and composition can be used to maximize the OER activity.<sup>[11–15]</sup> However, the synthesis of PBAs with tailored structures and the elucidation of the mechanism underlying catalytic efficiency and stability remain serious challenges.

Bearing this in mind, FeMn@CoNi core-shell PBAs were used as starting materials in this work. Low-temperature pyrolysis of FeMn@CoNi PBA together with Se powders was carried out in an argon (Ar) atmosphere. This proposed synthesis strategy enables the control of both the morphology and composition of the PBAs using a "one-stone-three-birds" approach. Specifically, this approach allows, in one pot, the formation of hollow interiors, the deposition of Ni nanoparticles (NPs) at their surface, and Se incorporation on the PBA structure. This enabled three main processes to take place: i) the partial dissociation of inner FeMn PBAs to yield a hollow interior, ii) Ni NPs exsolution to the surface generating Ni NPs, and iii) Se incorporation onto the PBA shell. These features endow our PBA materials with excellent OER activity under alkaline conditions, outperforming commercially available catalysts and most PBA-related state-of-the-art electrocatalysts. Besides, these new-design PBA catalysts exhibit robust long-term stability at 100 mA cm<sup>-2</sup> for 30 h. The subsequent electrochemical catalytic experiments, coupled with density functional theory (DFT) calculations and surface characterization, showed that the exsolved Ni NPs promoted the formation of Se-doped core-shell metal oxyhydroxides during the OER under alkaline conditions, in which the heterojunction with Ni and the Se incorporation improved the OER kinetics. We believe that our data can pave the way for the development of efficient OER catalysts by combining synthetic control over morphological and compositional features and understanding catalytic enhancement pathways.

#### 2. Results and Discussion

PBAs are characterized by their high metal centers/clusters and cyanide ligands and can be described by a chemical formula  $A_xM_1[M_2(CN)_6]_y \cdot nH_2O$  (where A represents alkali metals and  $M_1/M_2$  represents transition metals).<sup>[10]</sup> In PBAs, morphological and compositional features can be tailored to enhance catalytic activity. For example, the introduction of a hollow interior can increase the surface-to-volume ratio, but to do so, conventional synthesis methods necessitate multiple steps and rely on either chemical etching or expensive templates.<sup>[15]</sup> Another strategy involves anchoring metal NPs at their surface, helping improve catalytic activity (e.g., via the formation of heterojunctions).<sup>[16]</sup> This often requires multiple deposition steps and can lead to NPs agglomeration.<sup>[17]</sup>

In situ, metal exsolution has been used to overcome these limitations.<sup>[18]</sup> Metal exsolution refers to a process in which discrete NPs come out of a solid solution and anchor on the surface of the material.<sup>[18]</sup> This typically occurs during thermal treatments that provide energy for changes in the material's composition or structure. During exsolution, the metal atoms can selectively precipitate from the solid solution, forming small islands or NPs on the surface.<sup>[19]</sup> Normally, the exsolution process takes place under strong reduction conditions (such as Ar/H<sub>2</sub> atmosphere).<sup>[17,18]</sup> However, these conditions could trig-

ger a structural collapse and compositional segregation, which is detrimental to the synthesis of PBAs with desired features.<sup>[20]</sup> To date, the metal exsolution from PBA-based materials remains challenging without additional derivatives and under mild conditions. Another strategy to enhance catalytic efficiency is by tuning the electronic properties of PBAs via doping.<sup>[21]</sup> In this context, anion regulation has been reported to enable highperforming PBA OER electrocatalysts by charge transfer, in addition to optimizing the adsorption/desorption response of oxygencontaining intermediates on the catalyst surface.<sup>[22,23]</sup>

Based on this progress, we aimed to develop PBAs displaying superior OER efficiency and stability benchmarked against leading-edge electrocatalysts by combining hollow interiors, Ni NPs exsolution, and Se incorporation in a single synthetic step: one stone three birds strategy approach. Specifically, we adopted a low-temperature pyrolysis protocol that enabled us to obtain hollow interior, metal NPs at the PBAs surface via metal exsolution, and doping in a single step, employing mild conditions, and without any extra additives.

For the rational design of the composition, we focused on obtaining Ni NPs (earth-abundant metal with high OER activity) at the PBAs surface and, at the same time, employed Se as the dopant for PBA (Scheme 1). To achieve this, we chose core-shell FeMn@CoNi PBAs nanocubes as starting materials to produce hollow Ni/FeMn@CoNiSe nanocages (note that Ni NPs were decorated at the surface of hollow FeMn@CoNi-Se PBAs, where the outer CoNi shell was incorporated with Se). The starting FeMn@CoNi PBAs nanocubes (Figure S1, Supporting Information, the edge length of  $127 \pm 21$  nm) were prepared by a coprecipitation method, and the precursor was denoted as PBA-P.<sup>[20]</sup> The presence of CoNi PBA in the shell and FeMn PBA in the core is due to their different formation (nucleation and growth) rates, in which FeMn PBA is formed first, generating the core, followed by CoNi PBA which is then deposited at the surface of the pre-formed FeMn PBA.<sup>[20]</sup>

The hollow Ni/FeMn@CoNiSe nanocages could be prepared in one step by mixing PBA-P with Se powder followed by pyrolysis at 350 °C in an Ar atmosphere. For clarity, this material was named as PBA-Se 350. Here, as the core PBAs obtained in the first stage of the synthesis are expected to contain more defect sites, they are more susceptible to dissolution during the pyrolysis step.<sup>[15]</sup> Therefore, this enables their selective dissolution to yield a hollow interior under our proposed conditions. Two control samples were also prepared with such purposes: i) to reveal the role of Se in the electrolysis of water, the pyrolysis was carried out in the absence of Se (producing sample PBA-Ar 350), and ii) to ascertain the effect of metal exsolution on the catalytic operation, the pyrolysis was performed at a lower temperature (300 °C) in which metal exsolution would not take place (producing sample PBA-Ar 300).

The morphological and compositional features of the PBA-Se 350 nanocages (Ni/FeMn@CoNiSe) were investigated using electron microscopy (Figure 1). The scanning electron microscopy (SEM) image (Figure 1a; Figure S1, Supporting Information) reveals the samples' cubic shape and relatively uniform edge length  $(121 \pm 22 \text{ nm})$ . Transmission electron microscopy (TEM) images (Figure 1b,c) show the formation of a hollow interior within the cubic nanocages. It can be observed that the initial PBA framework remained stable during pyrolysis.



Furthermore, TEM images revealed the uniform distribution of small NP islands (sizes below 15 nm) decorating the surface of PBA-Se 350 nanocages. These NPs islands were presumably generated at the surface due to Ni exsolution from the CoNi PBA during pyrolysis. To confirm this, the selected-area electron diffraction (SAED) pattern and high-resolution TEM (HRTEM) images were obtained. As displayed in Figure 1c, the two sets of electron diffraction patterns can be assigned to PBAs and metallic Ni.<sup>[24,25]</sup> The HRTEM analyses of the FeMn core and CoNi shell regions (shown in red and yellow, respectively, in Figure 1d) reveal



Figure 1. a–g) Electron microscopy images for the PBA-Se 350 nanocages (Ni/FeMn@CoNiSe): a) SEM, b) TEM, c) TEM with corresponding SAED pattern, d) HRTEM, e) HRTEM of the I and II areas as seen in (d), f) HAADF-STEM images for the surface of PBA-Se 350, and g) STEM-HAADF of the whole particle with their corresponding STEM–EDS elemental maps. The elemental distributions of Fe, Co, Mn, Ni, and Se are shown in green, yellow, magenta, blue, and orange, respectively.

characteristic crystalline lattice spacings of FeMn and CoNi PBAs (Figure 1e). The HRTEM images in Figure 1e together with highangle annular dark-field scanning TEM (HAADF-STEM) images also reveal lattice fringes with interplanar spacings of 0.205 nm, corresponding to the (111) diffraction planes of metallic Ni.

The STEM-EDS elemental mapping (Figure 1g) shows the incorporation and uniform distribution of Se into PBA-Se 350 nanocages during the synthesis. Here, the 350 °C temperature enabled the controlled decomposition of the FeMn PBA core during the synthesis, leading to the formation of a hollow interior.<sup>[20,26]</sup> The thermogravimetric analysis (TGA) was used to probe the decomposition behavior of the PBA-P precursor in an Ar atmosphere (Figure S3, Supporting Information). The data collected showed structural evolution during calcination (up to 600 °C), including the dehydration process (under 150 °C), FeMn PBA core decomposition (starting at 200 °C), in situ exsolution of Ni NPs (>300 °C), and eventual structural collapse due to massive exsolution, resulting in overgrowth (starting at 400 °C). Thus, 350 °C represents the optimal sintering temperature at which the desired morphological and compositional features in PBA-Se 350 can be obtained (i.e., Ni/FeMn@CoNiSe). During the pyrolysis process, the exsolution behavior of PBAs materials is associated with the vacancy formation and diffusion dynamics of various metal sites.<sup>[18,19]</sup> This may explain why the Ni atoms have exsolved more favorably than the other metal atoms. The mechanistic understanding of the controllable metal exsolution in the PBAs material remains challenging. We have tried to gain further insights into the Ni exsolution process by performing thermodynamic (DFT calculations) and kinetic analysis (molecular dynamics simulations). It is plausible that CN vacancies in the bulk PBAs (denoted as  $V_{CN}$ ) formed during thermal treatment could drive the Ni exsolution similarly to the exsolution of B-site elements reported in perovskite oxides driven by O vacancies.[18,19] Figure S4a (Supporting Information) shows a scheme for  $V_{CN}$ configurations in the reported PBA materials. Our DFT calculations show that the V<sub>CN</sub> formation energy in the CoNi PBAs model was lower than that of the FeMn PBAs model, indicating the more favorable generation of  $\mathrm{V}_{\mathrm{CN}}$  in CoNi PBAs (Figure S4b, Supporting Information). Then, the formation energies of various metal vacancies (denoted the V<sub>M</sub>) were considered to evaluate the exsolution tendency, which might be the starting point of any metal site exsolution. It is surprising that all the V<sub>M</sub> formation energies decreased with the presence of  $\mathrm{V}_{\mathrm{CN}}$  , indicating that the V<sub>CN</sub> likely facilitates metal exsolution. Among all the metal sites,  $V_{\rm Ni}$  displayed the lowest vacancy formation energy and thus the greater tendency for exsolution. Molecular dynamics simulations at different temperatures were used to investigate atomic diffusion dynamics. Ni atoms exhibited higher mean square displacements (MSD) than Co, Fe, and Mn atoms at the initial step of the annealing process (450 and 550 K, Figure S4c, Supporting Information). This data suggests that Ni atoms could move more effectively in the bulk PBAs and undergo exsolution. With the increased temperature (650 K), the MSD value of Ni was lower than those of the other metals, suggesting the completion of Ni exsolution and stability of exsolved Ni NPs. Meanwhile, Mn might begin to exsolve due to the large MSD value, which was consistent with the TGA and TEM results (Figure S3, Supporting Information, the integral structure is destroyed at 450 °C with more exsolution of metallic nanoparticles).

The control samples (PBA-300 and PBA-350) were also investigated by SEM and TEM (Figure S5, Supporting Information), including STEM-EDS elemental mapping (Figure S6, Supporting Information), to ascertain the effect of the Se addition (PBA-350) and the suppression of the Ni exsolution (PBA-300) over the compositional and morphological developments. No Ni NPs were detected on the surface of the PBA-300 sample, whereas the exsolution of nickel from the PBAs became evident at 350 °C, similar to what was observed for PBA-Se-350. These findings indicate that a pyrolysis temperature of 350 °C is necessary to promote the exsolution of nickel from the PBAs. Moreover, the formation of a hollow interior at the particle center was less pronounced at 300 °C, indicating that 350 °C was essential for the formation of the hollow center. All the PBA-derived materials (PBA-Se 350 and control samples PBA-300 and PBA-350) were also interrogated by powder X-ray diffraction (XRD), Raman, UV-vis, X-ray photoelectron spectroscopy (XPS), and electron spin resonance (ESR) (Figure S7, Supporting Information), supporting the results from the electron microscopy analysis.

The PBAs materials are known to contain CN vacancies. The effect of Se doping on the suppression of CN vacancies in Prussian blue analogs was examined by comparing the ESR spectra of PBA-Se 350 and PBA 350 samples (Figure S7i, Supporting Information). The results showed a decrease in the ESR signal of PBA-Se 350 compared to that of PBA-Ar 350, demonstrating the effectiveness of Se doping in suppressing the formation of CN vacancies, possibly through the filling of Se atoms in the sites of CN vacancies. The DFT calculations (Figure S8, Supporting Information) support these findings, showing that isolated Se atoms tend to be adsorbed on the CN vacancy sites rather than the metallic Ni sites.

These results show the formation of a hollow core-shell FeMn@CoNi PBA structure in which the outer CoNi shell is doped with Se and Ni NPs decorated at the surface. These features (hollow interiors, Se dopant, and surface Ni NPs) make this material (PBA-Se 350) attractive as a catalyst for the OER in water splitting. To assess its OER activity, commercial RuO<sub>2</sub> electrocatalysts with a mass loading of 0.27 mg cm<sup>-2</sup> were deposited onto the nickel foam (NF) and used as a reference. PBA-Ar 300 and PBA-Ar 350 were also used as control electrocatalysts to unravel the effect of the Se doping and the presence of Ni NPs at the surface on the catalytic performance. The linear sweep voltammetry (LSV) curves in Figure 2a demonstrated that PBA-Se 350 achieved a current density of 10 mV cm<sup>-2</sup> with only 184 mV, while PBA-P, PBA-Ar 300, PBA-Ar 350, and RuO<sub>2</sub> required overpotentials of 241, 237, 216, and 338 mV, respectively (Figure 2b). All PBA electrocatalysts produced from the pyrolysis step in this work outperformed the initial PBA-P and RuO<sub>2</sub> systems. At an overpotential of 300 mV (Figure 2c), PBA-Se 350 exhibited the highest mass activity (762.32 A  $g^{-1}$ ), significantly outpacing PBA-P (95.04 A g<sup>-1</sup>), PBA-Ar 300 (130.63 A g<sup>-1</sup>), PBA-Ar 350 (298.15 A  $g^{-1}$ ), and RuO<sub>2</sub> (18.92 A  $g^{-1}$ ). These data suggest that the strategy proposed herein is promising to improve OER performance, especially given the high price and scarcity of RuO2.<sup>[27]</sup> Tafel plots were calculated from the obtained LSV curves to investigate OER kinetics during the electrochemical reaction (Figure 2d). PBA-Se 350 had a much lower Tafel slope value of 43.4 mV dec<sup>-1</sup> than the other samples, indicating the fastest OER processes. Using the Butler-Volmer equation, the

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**Figure 2.** The OER performance of PBA-Se 350 compared with PBA-Ar 350, PBA-Ar 300, PBA-P, and  $RuO_2$  electrocatalysts: a) the OER polarization curves; b) the comparison of the overpotential at 10 mA cm<sup>-2</sup>; c) the mass current density calculated at an overpotential of 300 mV; d) the Tafel plots derived from the OER polarization curves in (a); e) EIS Nyquist plots (scatters and lines represent the experimental and simulated data). Inset shows the equivalent circuit diagram; f) the electrocatalytic activity and special structural/compositional characteristics comparison among the PBA-P, PBA-Ar 300, PBA-Ar 350, and PBA-Se 350; g) the comparison of the overpotential (at 10 mA cm<sup>-2</sup>) and Tafel slopes of as-prepared PBA-Se 350 with alkaline OER catalysts reported by others (see also in Table S1, Supporting Information); h) the multi-current responses for the PBA-Se 350 electrocatalyst; and i) the stability test performed at 100 mA cm<sup>-2</sup> for 30 h.

exchange current density of the PBA-Se 350 electrode was calculated to be 2.65 mA cm<sup>-2</sup>, which was superior to that of  $RuO_2$  (1.79 mA cm<sup>-2</sup>), suggesting enhanced bonding/charge transfer at the reaction interface.<sup>[28]</sup>

The electrochemical double-layer capacitance ( $C_{\rm dl}$ ), a measure of the electrochemically active surface area, was determined and referenced when comparing the catalytic performance of the PBA materials.<sup>[28]</sup> As depicted in Figure S9, Supporting Information, PBA-Se 350 exhibits a  $C_{\rm dl}$  value of 6.09 mF cm<sup>-2</sup>, which is comparable to that of PBA 350 (5.41 mF cm<sup>-2</sup>) but superior to those of PBA-P (3.28 mF cm<sup>-2</sup>) and PBA-Ar 300 (4.79 mF cm<sup>-2</sup>), which were also consistent with the Brunauer–Emmett–Teller surface area results (Figure S10, Supporting Information). This observation suggests that the hollow structure and exsolved NPs on the surface of PBA-Se 350 provide more exposed active sites than the initial PBAs or the PBAs in which exsolution did not take place

(PBA-Ar 300). The unit activity was also calculated by normalizing the LSV curves by the obtained ECSA values as described in (Figure S11a, Supporting Information). As shown in Figure S11b (Supporting Information), the current density of PBA-Se 350 at an overpotential of 300 mV was larger relative to the other samples. Furthermore, the electrochemical impedance spectroscopy (EIS) data were collected under an overpotential of 300 mV. This value was chosen for the EIS experiments as this corresponds to catalytic turnover conditions, which is suitable to study the charge transfer resistance and OER kinetics of the catalysts.<sup>[18]</sup> The obtained EIS results were fitted based on the equivalent circuit, as shown in Figure 2e. As depicted in Table S1 (Supporting Information), the  $R_{ct}$  of PBA-Se 350 is significantly lower than those from other PBA materials and RuO<sub>2</sub>, indicative of a remarkable charge transfer ability consistent with the Tafel plot results.

We compared the electrochemical benchmark parameters on performance (such as  $\eta_{10}$ , Tafel slope, mass activity, and  $R_{\rm CT}$ ) among all PBAs materials to understand how the distinct compositional and structural features of the prepared PBAs affect the OER performance. These results are depicted in Figure 2f. The hollow interiors, Ni exsolution, and Se incorporation could separately promote the OER performance, endowing PBA-Se 350 the highest activity due to the combination of these three contributions. However, the exact degree of contribution or quantification of each factor on activity and stability is difficult to disentangle.

To further evaluate the electrocatalytic performance of PBA-Se 350, the overpotential at 10 mA cm<sup>-2</sup> and Tafel plots were compared with other reported catalysts (including core–shell-like, PBA-based, Se-doped, and noble-metal-based samples) as shown in Figure 2g and Table S2 (Supporting Information). The PBA-Se 350 catalyst exhibits excellent electrocatalytic activity compared to a variety of recently reported materials. Its superior OER performance could be attributed to the combination of unique morphological and compositional features, including effective anionic regulation (via Se doping), increased exposure of active sites (due to the hollow interior), and the presence of Ni NPs.

The operational stability of the PBA-Se 350 electrode was assessed using multi-step chronopotentiometry and long-term chronopotentiometry measurements, as shown in Figure 2h,i, respectively. The data collected show steady responses (Figure 2h) and excellent stability without significant performance deterioration during the continuous testing period under a current density of 100 mA cm<sup>-2</sup> (Figure 2i). The LSV curve of the PBA-Se 350 electrode following the stability testing was found to shift slightly toward higher voltages without severe performance degradation (Figure S12, Supporting Information). The decrease in the oxidation peak and the right shift of the LSV curves were caused by the electrode polarization after the long-term stability test under high current density. For our catalyst, under higher current density, excessive oxidation might cause a decrease in the oxidation peak or an increase in the overall resistance. It inevitably occurs on electrocatalysts. Even so, our catalysts still displayed no obvious attenuation, thus, we concluded that our catalyst has good stability. Furthermore, the Faradaic efficiency of the catalyst for the OER tests (at 100 mA cm<sup>-2</sup>) was close to 98% (Figure S13, Supporting Information), indicative of the high current utilization for the OER.<sup>[29]</sup>

To evaluate the practical application of the PBA-Se 350 electrocatalyst, it was employed as both the anode and cathode immersed in the electrolyzer for the overall water-splitting reaction. Commercial Pt/C and RuO<sub>2</sub> were also used as comparisons (anode and cathode, respectively). Notably, PBA-Se 350 electrodes exhibited superior performance for overall water splitting relative to Pt/C||RuO<sub>2</sub> cell (Figure S14, Supporting Information).

Next, we set out to unlock the catalytic mechanism that underlies the high OER activities observed in the PBA-Se 350 catalysts, by combining steady-state cyclic voltammetry (CV, **Figure 3**a), Fourier-transformed ac voltammetry (FTACV, Figure 3b), in situ Raman spectroscopy (Figure 3c), HRTEM (Figure 3d), XPS (Figure 3e), and DFT calculations (Figure S15, Supporting Information). As depicted in Figure 3a, the anodic and cathodic waves were observed in a potential range of 1.1–1.4 V (vs RHE) in the steady-state CV scans, which was lower than the onset potential. The dynamic surface reconstruction of the catalysts might take place at the active metal sites before water oxidation, as deduced from the oxidation peaks assigned for the oxidation of Ni<sup>2+</sup> to higher valence states (Ni<sup>3+</sup>/<sup>4+</sup>) accompanied by hydroxyl deprotonation. The redox potentials for Co<sup>2+</sup>, Mn<sup>3+</sup>, and Fe<sup>3+</sup> were much larger. The variation in the oxidation peak position for different PBA catalysts indicates the diverse evolution kinetics of active species. Moreover, the characteristic peaks for different PBA catalysts suggested that the surface reconstruction path varied significantly, with PBA-Se 350 showing the most rapid response compared to its counterparts.<sup>[30]</sup>

This observation was further supported by FTACV studies (Figure 3b), in which the high-order harmonic components were capable of effectively discerning the currents generated by catalytic reactions from the background charging current.<sup>[31]</sup> Figure 3b presents the 6th harmonic FTACV components for PBA-Se 350, PBA-Ar 350, PBA-Ar 300, and PBA-P, indicative of three distinct zones. Zones I and II correspond to the oxidization of diverse metal-based sites, leading to the formation of highvalent metal active centers. Zone III relates to the rapid OER, resulting in the generation of O<sub>2</sub> under increasing applied voltage. The PBA samples produced after pyrolysis exhibit a significant increase in current in Zone II, suggesting the presence of highly active  $M^{n+/(n+1)+}$  sites. The PBA-Se 350 sample displays the highest peak and the lowest onset potential, which is similar to PBA-Ar 350 but superior to PBA-Ar 300 and PBA-P. This is presumably due to the rich redox properties of various active metal sites.

The Ni NPs at the surface and the introduced metal-PBA interfaces were found to play a crucial role in accelerating the OER process. The DFT calculations (Figure S15, Supporting Information) showed that there is enhanced charge redistribution between Ni clusters and the CoNi-Se PBA (Figure S15a, Supporting Information). The planar average differential charge density of Ni clusters and the CoNi–Se PBA in the z-direction was also shown in Figure S15a (Supporting Information), indicating the possible formation of an enhanced internal electric field. This hypothesis was further demonstrated by the calculated work functions  $(W_{\rm F})$  of CoNi-Se PBA with/without Ni loading (Figure S15b, Supporting Information). The decreased work function after the combination with the Ni cluster suggested a higher Fermi level  $(E_{\rm F})$  level and a smaller  $W_{\rm F}$  of the Ni cluster. The contact-induced charge redistribution around the interface guarantees the electron transfer from the Ni clusters to CoNi-Se PBA. This interaction could alter the adsorption/desorption behavior of reaction intermediates (especially for the OH<sup>-</sup> species) and enhance surface reconstruction kinetics.<sup>[4]</sup> Moreover, the projected density of states (PDOS) for Ni 3d orbitals revealed an upshift of the d-band center of Ni atoms over the Ni/CoNi-Se PBA heterointerface toward the Fermi level  $(E_{\rm F})$  compared to pure CoNi–Se PBA (Figure S15c, Supporting Information). This upshift is believed to lead to an increase in empty antibonding states above  $E_{\rm F}$ , enhancing the interaction of Ni sites and OH<sup>-</sup> species and thus facilitating the formation of metal (oxy)hydroxides which are key to the OER performance. To quantitatively estimate the interaction intensity between Ni and OH<sup>-</sup> species, the projected crystal orbital Hamilton population (pCOHP) of Ni-O (Ni in the surface site and O in adsorbed \*OH) was further calculated. The integral COHP value (ICOHP) could be calculated by integrating the partial COHP below the  $E_{\rm F}$ , suggesting the number of bonded electrons between the selected

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**Figure 3.** a) Steady CV scanning and b) 6th-harmonic FTACV curves for PBA-Se 350, PBA-Ar 350, PBA-Ar 300, and PBA-P samples. c) Electrochemical in situ Raman spectra of PBA-Se 350 in the range of 300–800 cm<sup>-1</sup> as a function of applied potential. d) HRTEM, SAED pattern, HAADF-STEM, and STEM–EDS images for the PBA-Se 350 catalyst after the OER test with corresponding FFT/IFFT patterns of regions I and II. e) XPS spectra of the Fe 2p, Co 2p, Ni 2p, and Mn 2p (from left to right) for the PBA-Se 350 sample before (top trace) and after (bottom trace) the OER test.

Ni and O atoms and the corresponding bonding strength.<sup>[4]</sup> It was clear that the ICOHP of Ni–O in Ni/CoNi–Se PBA is larger than that of CoNi–Se PBA and indicated the stronger adsorption of OH<sup>-</sup> species (Figure S15d, Supporting Information). In summary, these results demonstrated that the loading of metallic Ni could facilitate the initiation of surface reconstruction.

To investigate the dynamic rearrangement behavior of the PBA-Se 350 catalyst during the OER process, the in situ Raman spectra were acquired in 1.0  $\times$  KOH electrolyte, with an applied voltage ranging from 1.1 to 1.6 V (vs RHE) (Figure 3c). At the beginning of the electrocatalytic process (1.1 V), two characteristic Raman signals centered  $\approx$ 445 and 521 cm<sup>-1</sup> were observed, which corresponded to the A<sub>1g</sub> stretching modes of Ni(OH)<sub>2</sub>.<sup>[32]</sup> As the voltage was increased to 1.3 V, these signals disappeared, and two new peaks were detected at 485 and 559 cm<sup>-1</sup>. They can be assigned to the  $E_{\rm g}$  bending vibration  $\delta$ (NiIII–O) and A<sub>1g</sub>

stretching vibration v(NiIII–O) in NiOOH, respectively.<sup>[32]</sup> The appearance of these peaks was consistent with the previous CV and FTACV results, confirming the oxidation of Ni into MOOH (metal oxyhydroxides). When the voltage reached 1.5 V, a blue shift and broadening of the peaks were detected due to the formation of MnOOH.<sup>[33]</sup>

Electron microscopy and XPS were employed to further characterize the morphological and compositional changes and gain insights into their impact on the catalytic efficiency of the PBA-Se 350. Figure 3d shows that the PBA-Se 350 catalyst retained its hollow feature post-test. However, a change in the morphological and compositional features was detected, since Ni NPs cannot be seen at the surface. The SAED pattern was composed of two sets of rings that can be assigned to NiOOH and MnOOH. The HRTEM coupled with fast Fourier transformation (FFT)/inverse FFT studies also shows lattice fringe spacings of 0.225 and 0.246 nm that can be indexed to NiOOH and MnOOH, respectively. Moreover, the PBA-Se 350 features a uniform distribution of the different elements. Figure S16 (Supporting Information) shows the EDS line scans obtained from STEM images before and after the OER test, confirming that the post-test PBA-Se 350 catalyst still maintained the core–shell structures. Also, the sample retained similar metal element distribution before and after the OER tests (Fe and Mn distributed in the inner regions, while the Co, Ni, and Se gathered in the outer parts). The peaks of O increased after the OER test, which strongly supported the in situ Raman and HRTEM results. The EDS and inductively coupled plasma mass spectrometry results also illustrate the changes in the relative atomic ratio after the OER test (Table S3, Supporting Information).

The XPS spectra of the catalyst (Figure 3e) also display significant differences before and after the OER testing. An increase in the number of peaks assigned to the oxidation of the species was detected. For instance, the peaks of the Fe<sup>2+</sup> component in the Fe 2p spectra were partly oxidized to Fe<sup>3+</sup>. Similarly, the Co<sup>2+</sup> species completely disappeared and evolved into Co<sup>3+</sup> in the Co 2p spectra. In the Ni 2p core levels, the spectra could be resolved into three components. First, the disappearance of the Ni<sup>0</sup> peak indicates that the metallic Ni NPs were efficiently oxidized to a higher valence Ni-O species during the reaction process. Additionally, Mn<sup>2+</sup> was found to be slightly oxidized. In the case of Se, the XPS signal was detected for the Se 3d spectrum (Figure S17, Supporting Information), which can be ascribed to Se-O species, suggesting the incorporation of Se into the reconstructed product. Meanwhile, the O 1s XPS spectrum shifted toward the negative position connected with the formation of the M-OOH/M-O bond from the hydroxide or (oxy)hydroxide, as shown in Figure S18 (Supporting Information).<sup>[30]</sup>

These results indicate that, after the OER testing, the PBA-Se 350 consists of Se-doped metal (oxy)hydroxides possessing a hollow heterojunction structure composed of Mn(Fe)OOH@Sedoped Ni(Co)OOH. Based on this understanding, a mechanistic model was formulated to explain the OER performance, which is based on: i) the extensive adsorption of dissociative OH<sup>-</sup> species (from the alkaline solution) over the Ni–PBAs interfaces; ii) the conversion of Ni NPs and outer Se-doped CoNi PBA into Ni(Co)OOH—Se, and iii) the inner FeMn PBAs converted into Mn(Fe)OOH to produce the heterojunction, as illustrated in Figure S19 (Supporting Information). It is believed that these Semodified hollow metal (oxy)hydroxides promoted OER kinetics and stability.<sup>[34]</sup>

The modeling analysis was carried out to unravel the origin of the enhanced OER performance in the reconstructed PBA-Se 350 catalyst produced during the OER. The model of the resultant Mn(Fe)OOH@Ni(Co)OOH-Se heterojunction was proposed (Figure S20, Supporting Information). Ni(Co)OOH, Ni(Co)OOH—Se, and Mn(Fe)OOH@Ni(Co)OOH units were chosen for the modeling analysis. As displayed in Figure S21 (Supporting Information), the total density of states (TDOS) for Mn(Fe)OOH@Ni(Co)OOH—Se was calculated and found to be larger than those of Ni(Co)OOH, Ni(Co)OOH—Se, and Mn(Fe)OOH@Ni(Co)OOH. This suggests that the electrontransfer rate (and catalytic activities) could be promoted by the formation of the heterointerface and Se incorporation.<sup>[35]</sup> Furthermore, the PDOSs of various constituent elements in the Mn(Fe)OOH@Ni(Co)OOH-Se model were determined and used to probe the local electronic structures (Figure 4a). The Fe-3d orbitals were located at deeper positions far away from the  $E_{\rm r}$ . resulting in ample electron-rich sites. The Mn-3d orbitals exhibit a broad range of distribution in the valence band and strongly overlap with Ni-3d orbitals, indicative of the efficient d-d coupling over the interfaces to accelerate electron transfer.<sup>[36]</sup> The Ni and Co sites were buried at closer positions near  $E_{\rm F}$ , demonstrating the rapid electron-transfer capability and the stable adsorption of the intermediates during the OER, indicative of high electroactivity. The p orbitals of Se show a wide range and cross the  $E_{\rm F}$ . It coincides well with the TDOS results, indicative of enhanced conductivity. O sites also cover a broad range and are strongly coupled with metal 3d orbitals, which could enhance the site-to-site electron transfer. To forge an in-depth understanding of the potential active metal sites, the site-dependent PDOSs of Ni and Mn sites are provided in Figure 4b,c. From the single Ni(Co)OOH-Se model to the interfacial sites of the heterojunction, the Ni 3d orbitals exhibit an upshifting trend, indicative of the more electron-rich nature and higher valence states at the interface, which could boost the electron transfer from the active sites to the adsorbates to promote the OER kinetics. In the meantime, the  $e_g$ - $t_{2g}$  of Mn-3d orbitals present a trend of nearly linear increase from the bulk to the surface. This phenomenon endows better modulation of the valence states of Ni.[37] The charge density difference was also examined to verify the potentiation of the heterointerface. As displayed in Figure 4d, the charge distribution between Ni(Co)OOH-Se and Mn(Fe)OOH was altered, resulting in charge transfer. It could further regulate the adsorption capability of reaction intermediates on the electrocatalysts, thus optimizing the OER process.

Apart from the intrinsic electronic structure, we also investigated the variation in the adsorption and conversion of vital OER intermediates. The  $\sigma$  orbitals of O-containing orbitals were employed to uncover the electron-transfer process of adsorbed intermediates.<sup>[36]</sup> As shown in Figure 4e, from the first adsorption of \*OH toward the final product O<sub>2</sub> (\*OH $\rightarrow$ \*O $\rightarrow$ \*OOH $\rightarrow$ O<sub>2</sub>), the  $\sigma$  bonds of O sites gradually upshifted with a nearly linear correlation. This predicted rapid electron transfer with low barriers for efficient intermediate conversions during the electrocatalytic reaction. The energetic trends of the four OER steps were calculated concerning the different Ni sites in the proposed models over the (011) face to examine the energy barriers encountered in the electrocatalytic OER (Figure S22, Supporting Information). As depicted in Figure S23 (Supporting Information), without the bias potential (U = 0 V), the stepwise process shows a persistent uphill trend, indicative of an endothermic reaction.<sup>[36]</sup> For Ni(Co)OOH and Mn(Fe)OOH@Ni(Co)OOH, the largest energy barrier ( $\Delta G$ ) was noted for the conversion of \*OH to \*O, up to 1.79 and 1.68 eV, respectively, indicative of the rate-determining-step (RDS). On the other hand, the RDS for both Ni(Co)OOH-Se and Mn(Fe)OOH@Ni(Co)OOH was associated with the reaction from  $(*O + 2OH^- + H_2O)$  to  $(*OOH + OH^- + H_2O)$ . It was related to the diverse adsorption/desorption capacity caused by anionic modulation, which could be indirectly evaluated by dband centers (Figure S24, Supporting Information).<sup>[37]</sup> Notably, Ni sites on the Mn(Fe)OOH@Ni(Co)OOH-Se model show a much smaller energy barrier (1.51 eV) than other models,

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**Figure 4.** a) The PDOSs of Mn(Fe)OOH@Ni(Co)OOH—Se. b,c) Site-dependent PDOS of Ni (b) and Mn (c) in Mn(Fe)OOH@Ni(Co)OOH—Se.d) Charge density in Mn(Fe)OOH@Ni(Co)OOH—Se. Blue and yellow contours represent electrons accumulation and depletion, respectively, where the isosurfaces are set to 0.05 e Å<sup>-3</sup>. e) The PDOS of key adsorbates on Mn(Fe)OOH@Ni(Co)OOH—Se during the OER. f) Standard free energy diagram of the OER process at 1.23 V of Ni sites in various models.

supporting the excellent OER activity of PBA-Se 350 in experimental tests. Under the 1.23 V potential, the thermodynamic overpotentials of different electrocatalysts were calculated (Figure 4f). Unsurprisingly, the Ni sites in Mn(Fe)OOH@Ni(Co)OOH-Se exhibit the lowest overpotential (0.28 V) to execute the exothermic OER catalysis. The electron density difference with the adsorbed configuration of the RDS reaction (\*O) also suggests efficient charge transfer during the conversion process (Figure S25, Supporting Information). Therefore, the theoretical results have demonstrated that the optimized electronic structures and the adsorption/desorption of key intermediates were induced by the synergistic effect of Se modification, compositional variations, and the heterojunction during the OER. In summary, the unique architecture combined with the abundant highly active sites in the reconstructed phase guaranteed superior activity during OER catalysis.

### 3. Conclusion

A facile yet effective pyrolysis technique was formulated to produce a new type of core–shell PBAs for catalytic applications. Starting from FeMn@CoNi core–shell PBAs and Se powders, the synthesis process consisted of three steps: the decomposition of the inner FeMn PBAs, the exsolution of Ni NPs, and Se doping. The resulting PBA-Se 350 possesses a hollow interior with a high specific surface area. It contains an inner FeMn PBA core and an outer CoNi–Se PBA shell decorated with Ni NPs. The new material design exhibited an ultralow overpotential (184 mV) at 10 mA cm<sup>-2</sup> and remarkable stability for the OER, surpassing leading catalysts such as RuO<sub>2</sub>. The high OER performance was attributed to morphological and compositional changes during the OER that led to the formation of a highly active species, that is, Se-doped metal (oxy)hydroxides possessing a hollow heterojunction structure. The new formation can be described as Mn(Fe)OOH@Se-doped Ni(Co)OOH with copious heterojunction interfaces (surface area) and Se doping, which enabled the control over the electronic structure that could be used to tune adsorption/desorption energies. The results illustrate the importance of the controlled synthesis and morphological and compositional changes that are responsible for the enhanced OER activity during the OER. The findings thus offer important insights and may inspire future work for the development of highly active, hybrid electrocatalysts for energy conversion and storage applications.

## **Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

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## **Conflict of Interest**

The authors declare no conflict of interest.

## **Data Availability Statement**

The data that support the findings of this study are available from the corresponding author upon reasonable request.

### **Keywords**

catalytic mechanism, hybrid materials, metal exsolution, oxygen evolution reaction, Prussian blue analogues

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