Anodic Transformation of a Core-Shell Prussian Blue Analogue to a Bifunctional Electrocatalyst for Water Splitting

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Developing low-cost oxygen evolution reaction (OER) catalysts with high efficiency and understanding the underlying reaction mechanism are critical for electrochemical conversion technologies. Here, an anodized Prussian blue analogue (PBA) containing Ni and Co is reported as a promising OER electrocatalyst in alkaline media. Detailed post-mortem characterizations indicate the transformation from PBA to Ni(OH)₂ during the anodic process, with the amorphous shell of the PBA facilitating the transformation by promoting greater structural flexibility. Further study with operando Raman and X-ray photoelectron spectroscopy reveal the increase of anodic potential improves the degree of deprotonation of the transformed core-shell PBA, leading to an increase of Ni valence. Density functional theory calculations suggest that the increase of Ni valence results in a continuous increase in the adsorption strength of oxygen-containing species, exhibiting a volcano relationship against the OER activity. Based on the experiments and calculated results, an OER mechanism for the transformed product is proposed. The fully activated catalyst also works as the cathode and the anode for a water-splitting electrolysis cell with a high output current density of 13.7 mA cm⁻² when a cell voltage of 1.6 V applied. No obvious performance attenuation is observed after 40 h of catalysis.

1. Introduction

Energy storage and conversion technology based on water splitting and recombinanion is potentially the most effective and ideal zero carbon technology.[1–3] The anodic half-reaction in water splitting, the oxygen evolution reaction (OER), involves a multi-step proton-coupled electron transfer process, which makes the reaction intrinsically slow, thereby requiring an overpotential.[4–6] The application of benchmark anode electrocatalysts, such as IrO₂ and RuO₂ is limited due to cost issues.[7,8]

In recent years, researchers have explored the first row 3d transition metal oxides as low-cost OER catalysts.[9–11] For instance, it was reported that some cobalt-based oxide surfaces self-reconstruct to Co (III) oxyhydroxide in which the di-µ-oxo bridged Co–Co sites provide high activity.[12] Fabbri et al.[13] and Shao et al.[14] unraveled a dynamic reconstruction of the well-known Ba₆₋₂Sr₂₋₄Co₁₋₂Feₓ₂₋₄O₃₋₄ catalyst, revealing a (CoFe)O(OH) active layer. It was reported that Co₃O₄[15] and CoO₃[16] plus NiO,[17] NiFe,[18] and NiCo oxides,[9] operate in a similar manner when an anodic potential is applied.

Recently, Prussian blue analogues (PBAs), composed of metal centers/clusters and functional organic ligands, have been extensively studied as new materials for electrocatalysis.[19–21] As alternatives to metal-organic frameworks (MOFs), great efforts have been made to customize their shapes,[22,23] chemical compositions[24] and unsaturated surface atoms[25] to obtain well-defined chemical structures, readily accessible active sites and excellent mechanical properties.[26–28]

Studies have found that PBAs undergo similar surface reconfigurations to those of transition metal oxides.[16,21] The layer of oxides remaining after OER indicates that the actual catalysts are metal (oxy)-hydroxides, which show excellent OER reactivity under anodic conditions.[11,14] However, as PBAs are easily etched in acidic and alkaline solutions, their use as catalysts is limited. To circumvent this problem, it is highly desirable to develop strategies for maintaining transformations but preventing etching in these materials. Moreover, stable systems will allow investigation of the physical origin and evolution of the active sites of PBAs under OER conditions.

Herein, we investigate the transformation of a NiCo-PBA to a layered metal hydroxide by anodization in a basic solution. Two PBAs are considered, a simple crystalline NiCo-PBA and a crystalline NiCo-PBA with an amorphous NiCo-PBA shell designed to prevent disintegration of the material upon transformation. The as-formed materials are characterized in detail. The performance of the transformed core-shell PBA as an OER catalyst is analyzed and density functional theory (DFT) calculations are performed to rationalize its superior behavior.
2. Results and Discussion

2.1. Structural Evolution of PBAs

The synthesis procedure for the target materials is summarized in Figure 1. NiCo@A-NiCo-PBA was prepared by a facile topological growth method. Core crystals of NiCo-PBA were placed in a fresh solution containing metal ions, cyanogen linker, and citrate dihydrate capping agent for the in situ growth of A-NiCo-PBA shell to form the NiCo@A-NiCo-PBA composite. Subsequently, NiCo@A-NiCo-PBA was drop-coated onto a clean FTO substrate and activated by anodization in 1 M NaOH electrolyte at an applied voltage of 1.55 V versus RHE (Figure S1, Supporting Information). During anodization the current density dramatically decreased over the first minute and then maintained nearly a constant value for the remaining time. The sample after activation was denoted NiCo@A-NiCo-PBA-AA.

2.1.1. Pre-Transformation Structure Characterization

Figure 2 displays the structural analysis of as-prepared PBA samples before anodic treatment. TEM was employed to investigate the structure of NiCo-PBA (Figure 2a,b) and NiCo@A-NiCo-PBA (Figure 2c,d). It is observed that the PBA precursors possess regular cubic morphology, with NiCo-PBA exhibiting sharper corners compared to NiCo@A-NiCo-PBA. Moreover, the core-shell structure of NiCo@A-NiCo-PBA is clearly distinguishable. The thickness of the shell is ≈25 nm, with a clear interface between the NiCo-PBA core and the A-NiCo-PBA shell. This is because of the different crystallinity of the core and shell, where the core is single-crystal, and the shell is amorphous.

According to the FESEM image (Figure 2e), the size distribution of NiCo@A-NiCo-PBA is narrow. It is worth mentioning that the highly symmetric nanocube structure of the core-shell PBA ensures the same diffusion path of oxygen atoms starting from different outer surfaces. The inset of Figure 2e is the histogram of the particle size distribution, exhibiting the particle sizes in the PBAs before and after the synthesis of the shell. The mean particle dimension of NiCo-PBA is 277 nm, while it was increased to 311 nm after the addition of the shell, in agreement with the previous TEM results.

2.1.2. Post-Transformation Structure Characterization

The post-mortem investigations of the fully activated catalyst NiCo-PBA-AA and NiCo@A-NiCo-PBA-AA were performed to understand how anodization in 1 M NaOH at 1.55 V versus RHE alters the structural morphology. The SEM image (Figure S2a, Supporting Information) and TEM images (Figure S2b,c, Supporting Information) indicate that the nanocube shape of NiCo-PBA transformed into a nanocage after 5 min electrochemical processing. The etching proceeds preferentially along the diagonal, and a distinct cavity forms at the vertices of eight corners and converges in the center of the nanocube, consequently forming the hollow cage structure. It is worth noting that the etching was accompanied by the break-up of some particles. When the anodization was prolonged to 10 min (Figure S2d, Supporting Information), the nanocage structure was maintained, with porosity and an expanded particle volume. It is also clear that the degree of crystallization of NiCo-PBA-AA was lowered, providing evidence that amorphous crystals were formed. However, for NiCo@A-NiCo-PBA anodized in 1 M KOH at 1.55 V versus RHE, TEM (Figure S2e,f, Supporting Information) shows that initial cubic morphology was transformed to a spherical shape with irregular edges. About 30 nm from the edge of the nanoparticle is amorphous, with contrast evidently
lower than in the center of the particles. The SAED pattern and the HRTEM image (Figure S2f, Supporting Information, inset) exhibited a typical amorphous pattern, which is attributed to the amorphous shell on the surface of the particles. This illustrates that the PBA catalysts are transformed upon anodization. The difference of core and core-shell PBA upon anodization was attributed to the introduction of the amorphous shell to the particles.

The specific surface areas and pore size distribution of the core-shell PBA before and after the activation were measured by nitrogen adsorption-desorption analysis (Figure 2f and Figure S3, Supporting Information). Adsorption-desorption curves (Figure 2f) of NiCo@A-NiCo-PBA and NiCo@A-NiCo-PBA-AA both show a type II isotherm, indicating the co-existence of microspores and mesopores. The specific surface areas were calculated by the BET method. Anodized NiCo@A-NiCo-PBA-AA has a BET surface area of 179.12 m² g⁻¹, which is much larger than that of the parent NiCo@A-NiCo-PBA (45.33 m² g⁻¹). The pore-size distribution was calculated by the BJH method (Figure S3, Supporting Information). It revealed the sizes were centered at less than 1 and 3.44 nm in NiCo@A-NiCo-PBA-AA. The pore volume of the PBA after activation was raised from the 0.0283 cm³ g⁻¹ for NiCo@A-NiCo-PBA to 0.0518 cm³ g⁻¹ for the anodized sample, demonstrating the activation greatly promotes the specific surface area and changes the pore structure, improving the contact area of the interior structure of PBA with electrolyte.

2.2. Changing of Chemical Composition Through Transformation

To investigate the chemical composition, powder X-ray diffraction (XRD) was performed on the PBAs. The XRD patterns of the initial core and core-shell PBA are compared in Figure S4, Supporting Information, a broad peak ≈ 20° appears in NiCo@A-NiCo-PBA, indicating the addition of the shell increases the amount of amorphous phase. There is also a slight diffraction peak shift to low angle in NiCo@A-NiCo-PBA, indicating an increase of crystal cell parameters, hence the increase of interplanar spacing. It can be also observed that the diffraction peaks of the core-shell PBA become narrower than
that of the core PBA. The corresponding full width at half maximum for NiCo@A-NiCo-PBA and NiCo-PBA are 0.162°, 0.177° for (200) plane; 0.331°, 0.359° for (220) plane; and 0.307°, 0.328° for (400) plane, respectively. All three peaks display narrowing after the wrapping of the shell, indicating an increase in particle size.

XRD was further used to study the chemical transformation during the anodic activation. As displayed in Figure 3a, the diffraction peaks of the core-shell PBA precursor at 2θ = 17.9°, 25.4°, 36.3°, and 40.5° match well with the (200), (220), (400), and (420) crystalline planes of Ni₃[Co(CN)₆]₂·xH₂O (JCPDS card no. 221184), confirming the product is highly pure and has good crystallinity with a face-centered cubic structure. After 5 min of anodization, most of the core-shell PBA was converted to hexagonal Ni(OH)₂ (JCPDS card no. 140117), the two phases co-exist in the sample and the diffraction peaks match well with those of the simulated Ni₃[Co(CN)₆]₂·xH₂O (cyan)/Ni(OH)₂ (red). When the anodization time was increased to 10 min, the transformation was complete, the NiCo@A-NiCo-PBA was fully converted to Ni(OH)₂. In addition, the degree of crystallinity decreased with the anodization time, suggesting amorphization happens during the transformation.

Figure 3. Chemical composition analysis. a) XRD patterns of NiCo@A-NiCo-PBA, NiCo@A-NiCo-PBA-5 min and NiCo@A-NiCo-PBA-AA. b) FT-IR spectra of NiCo@A-NiCo-PBA, NiCo@A-NiCo-PBA-5 min and NiCo@A-NiCo-PBA-AA. XPS high-resolution spectra at c) C 1s edge, d) N 1s edge, e) O 1s edge and f) Ni 2p edge of NiCo@A-NiCo-PBA, NiCo@A-NiCo-PBA-5 min and NiCo@A-NiCo-PBA-AA. The spectra were shown with raw data and fitting data derived by Lorentz–Gaussian function.
However, for the core PBA, the transformation is much slower (Figure S5a, Supporting Information), under the same anodization conditions for 5 min, the major phase in the sample is PBA, and even after a 10 min anodization, some of the precursor PBA remains, indicating incomplete transformation. When the time was extended to 30 min (Figure S5b, Supporting Information), there was still residual PBA in the sample, proving that the transformation was difficult to complete in NiCo-PBA, after the anodization time was prolonged to 60 min, the reaction was finally completed (Figure S5b, Supporting Information).

The change in chemical composition during anodic transformation of core-shell PBAs was analyzed by FT-IR spectra, as shown in Figure 3b. The broad peak at 3416 cm$^{-1}$ corresponds to O–H stretching vibrations of residual physiosorbed water molecules, which remained consistent as the electrochemical treatment time increased.\(^{[28]}\) Over an anodization time from 0 to 10 min, it was observed that the C=O peak of Ni$_3$[Co(CN)$_6$]$_2$ at 2203 cm$^{-1}$ was significantly reduced and eventually disappeared, while the O=H peaks assigned to the stretching and bending vibrations in Ni(OH)$_2$ at 2116 and 1390 cm$^{-1}$, respectively, were strengthened.\(^{[30,31]}\) The peak at 1616 cm$^{-1}$ is due to the stretching vibrations of C–H. A similar trend was observed for NiCo-PBA (Figure S6, Supporting Information), where there is still a high intensity C≡N peak in Ni$_2$[Co(CN)$_6$]$_2$ after 10 min anodization, indicating there was still a large amount of PBA unconverted in the sample at this stage.

The composition evolution and valence state changes with anodization in the core-shell PBA are further supported by X-ray photoelectron spectroscopy (XPS). From the high-resolution XPS spectra in Figure 3c, it is observed that the fitted C 1s edge spectrum of the NiCo@A-NiCo-PBA revealed two main peaks at $\approx$284.8 and 285.4 eV corresponding to C–C and C–N, respectively.\(^{[32]}\) The fitted C 1s spectrum of the sample after 5 or 10 min anodization displays C–O–C bonds at 289.1 eV consistent with the transformation to Ni(OH)$_2$.\(^{[32]}\) The fitted N 1s peak (Figure 3d) of NiCo@A-NiCo-PBA was split into two peaks at 398.9 and 399.2 eV, which correspond to C≡N and pyrrolic nitrogen, respectively.\(^{[33]}\) Water molecules are easily adsorbed on pyrrolic nitrogen, leading to the shift to a high binding energy. The O 1s edge peaks (Figure 3e) of NiCo@A-NiCo-PBA at 530.9, 532.4, and 536.1 eV were assigned to Ni=O bonds, adsorbed oxygen species and C–O–C bonds, respectively.\(^{[34,35]}\) Notably, an additional peak at 531.9 eV emerged after 5 min activation, the peak was attributed to hydroxyl groups, while the peak of adsorbed oxygen species disappeared, this is because the conversion from PBA to Ni(OH)$_2$ requires the consumption of the adsorbed oxygen on the sample surface.\(^{[16]}\)

On increasing the anodization time to 10 min, another peak appears at 533.3 eV corresponding to oxygen vacancies and defects created during the anodization process. The Ni 2p edge peaks (Figure 3f) of NiCo@A-NiCo-PBA found at 855.7 and 873.2 eV were assigned to 2p$_{3/2}$ and 2p$_{1/2}$ spins of Ni$^{2+}$, and the two peaks at 856.9 and 874.3 eV were attributed to 2p$_{3/2}$ and 2p$_{1/2}$ spins of Ni$^{3+}$, indicating the co-existence of Ni$^{2+}$ and Ni$^{3+}$ in NiCo@A-NiCo-PBA. The relatively strong satellite peaks demonstrate the predominance of Ni$^{2+}$ in the near-surface region. After 5 min anodization, the peaks of Ni$^{2+}$ disappear, only Ni$^{3+}$ remained in the products. With the anodization time raised to 10 min, new peaks at 860.9 and 878.1 eV, attributed to Ni$^{2+}$ emerge.\(^{[32]}\) In NiCo@A-NiCo-PBA, two characteristic peaks of Co 2p are observed (Figure S7, Supporting Information) at binding energies of 782.1 and 797.2 eV which correspond to 2p$_{3/2}$ and 2p$_{1/2}$ spins of Co$^{2+}$, respectively. The N 1s and Co 2p XPS spectral peaks after 10 min anodization were both absent owing to the dramatic loss of Ni$_3$[Co(CN)$_6$]$_2$ in the sample, indicating the transformation from Ni$_3$[Co(CN)$_6$]$_2$ to Ni(OH)$_2$ was complete.

Figure 4 gives the HADDF image and the corresponding element mapping of core-shell PBA before and after the anodization process. The mapping result of NiCo@A-NiCo-PBA nanocube (Figure 4a–g) confirms the as-treated product contains C, N, O, Ni, and Co. After the electrochemical treatment, an even distribution of Ni and O elements on the residual catalyst is observed, while almost no N and Co signals were detected (Figure 4a–g). This observation was further confirmed by the energy-dispersive spectroscopy (EDS) data (Figure 4f,g). These findings suggest that the pristine core-shell PBA structure completely degraded into a partially amorphous structure containing Ni and O under anodization.

### 2.3. Insight into the Water Oxidation on PBAs

Cyclic voltammetry (CV) was used to probe O$_2$ evolution on NiCo@A-NiCo-PBA before and after anodization, as shown in Figure 5a. No peaks were observed in the CV observed prior to anodization, while after 5 and 10 min of anodization at 1.55 V versus RHE, the results display a typical electrocatalytic process for O$_2$ generation on Ni(OH)$_2$.\(^{[38]}\) There is one peak attributed to the Ni$^{2+}$→Ni$^{3+}$ process ($\approx$1.30 V) detected. This process happens together with the formation of the O*, which is an essential intermediate and couples with one OH$^-$ to generate *OOH for oxygen evolution.\(^{[39,40]}\) The displacement behavior of the CV indicates that the surface of the catalyst has undergone irreversible transformation to form hydroxides, and a catalytic surface with high OER activity was formed.

Figure 5b shows the CV curve of NiCo@A-NiCo-PBA-AA, and the inset shows the corresponding oxygen evolution intermediate pathways: at low potential (region I), *OH generation; in the mid potential (region II), the above-mentioned process occurs; and then O$_2$ generates under high potential (region III). The three simplified processes of water oxidation include *OH adsorption, *OH radical formation, and *OOH transformation and desorption.

The water oxidation performance comparison of PBAs is shown in Figure 5c,d. Linear sweep voltammetry measurements (Figure 5c) show that both NiCo@A-NiCo-PBA and NiCo-PBA have poor OER activity, and there is no obvious peak observed. By contrast, after activation (Figure 5d), the peak for the transformation of Ni$^{2+}$→Ni$^{3+}$ appears at $\approx$1.55 V. In order to eliminate the influence of the oxidation peak, chronopotentiometry test was performed on the core-shell PBA to accurately find the actual oxygen evolution reaction potential at a current density of 10 mA cm$^{-2}$, the results are shown in Figure S8, Supporting Information. Because of the existence of the oxidation peak (pseudo capacitance), the voltage rose gradually at the beginning, and then stabilized at 1.506 V, which is the potential
required for OER at a current density of 10 mA cm\(^{-2}\), and thus the accurate \(\eta_{10}\) is 276 mV. It is worth noting that the OER performance of the core PBA fully converted under 60 min of activation is worse than that of NiCo-PBA-AA under 10 min of activation (Figure S9, Supporting Information). Furthermore, the overpotentials of NiCo@A-NiCo-PBA-AA at current densities of 50 and 100 mA cm\(^{-2}\) are also listed in Figure 5f and Table S1, Supporting Information, which are 443 and 544 mV, respectively, far lower than those of NiCo-PBA-AA. This indicates the strengthened catalytic activity of NiCo@A-NiCo-PBA-AA is related to the presence of the amorphous shell. The Tafel slopes of PBAs after electrochemical treatment are shown in Figure 5e, the decreased Tafel slope of NiCo@A-NiCo-PBA-AA compared with NiCo-PBA-AA suggests a smaller overpotential is required to increase the current density ten times, indicating significantly enhanced activity of NiCo@A-NiCo-PBA after wrapping with an amorphous shell.

The mass activity of NiCo@A-NiCo-PBA-AA is 54.1 A g\(^{-1}\) at a quite small overpotential of 0.28 V, which is approximately eight times higher than NiCo-PBA-AA and twice than that of NiCo@A-NiCo-PBA (Figure 5g). To the best of our knowledge, the mass activity for our NiCo@A-NiCo-PBA-AA is the highest

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**Figure 4.** Chemical composition analysis. a\(_1\),a\(_2\)) HAADF-STEM image and EDS elemental mapping images of b\(_1\),b\(_2\) C K edge, c\(_1\),c\(_2\) N K edge, d\(_1\),d\(_2\) O K edge, e\(_1\),e\(_2\) Ni L edge, f\(_1\),f\(_2\) Co L edge and g\(_1\),g\(_2\) overlay (Scale bar: a,b: 400 nm). h\(_1\),h\(_2\) STEM-EDS of NiCo@A-NiCo-PBA and NiCo@A-NiCo-PBA-AA.
The enhanced catalytic activity of NiCo@A-NiCo-PBA-AA catalyst results from the amorphous shell and electrochemical activation.

To obtain more insight regarding the water oxidation process, an electrochemically active surface area investigation of NiCo@A-NiCo-PBA and NiCo@A-NiCo-PBA-AA was carried out. The characteristic CV curves with different scan rates are shown in Figure S10, Supporting Information. The slopes of NiCo@A-NiCo-PBA and NiCo@A-NiCo-PBA-AA are 7.83 and 4.52, respectively, where double-layer capacitance ($C_{dl}$) is half of the value, that is, 3.92 and 2.26 mF cm$^{-2}$, respectively (Figure 5h).

Multistep chronoamperometry was also carried out at potentials of 1.49, 1.68, and 1.73 V, as shown in Figure 5i, the results demonstrate that the current density at NiCo@A-NiCo-PBA-AA remains constant at each applied potential throughout the test, revealing a rapid response of carrier migration. After the voltage is increased and then restored to the original value, the current density returns to the initial level, indicating NiCo@A-NiCo-PBA-AA has strong structural and electrochemical stability after initial anodization, which proves that the transformation is completed in 10 min. It is worth noting the catalytic activity of this sample did not increase with increased anodization time (Figure 5i), demonstrating that the transformed materials are stable and the OER mechanism involving lattice oxygen is not dominant in this study. In the OER mechanism, dominated by lattice oxygen, cations on the catalyst are continuously leached as the number of cycles increases, which leads to an increase of catalytic activity.[44–47]

To detect the interfacial resistance of the corresponding process, electrochemical impedance spectroscopy was performed (Figure 5i, inset). The inset shows the equivalent electric circuit used. The values of the components that yield the best fit to the experimental data and the corresponding
error values are shown in Table S2, Supporting Information. It is found that the activated NiCo@A-NiCo-PBA exhibited lower series resistance ($R_s$) and charge transfer resistance ($R_{ct}$) compared with NiCo-PBA-AA, revealing the good charge transfer kinetics of the transformed core-shell material. Based on the above experimental results and analysis, NiCo@A-NiCo-PBA catalyst underwent an activation process during anodization, implying a transformation of the catalyst surface structures.

To unravel the mechanism of the transformation, analysis of PBAs subject to immersion in alkaline solution were conducted and the XRD patterns are shown in Figure S11, Supporting Information, it is found that the PBA etches and Ni(OH)$_2$ is formed without anodic potential (Equation (1)). This process is slow and the rate of conversion of PBA to Ni(OH)$_2$ is accelerated under anodic polarization comparing with the XRD of PBAs after anodization (Figure 3a and Figure S5, Supporting Information). Based on the XPS (Figure 6a–c) and operando Raman results (Figure 6d), it is observed the decrease of Ni$^{2+}$ species and the generation of Ni$^{3+}$ species as the anodized potential increases, indicating the establishment of Equation (2).

\begin{equation}
\text{Ni}_3\left[\text{Co}^{II}(\text{CN})_6\right]_2 + 6\text{OH}^- \rightarrow 3\text{Ni}^{II}(\text{OH})_2 + 2\left[\text{Co}^{II}(\text{CN})_6\right]^{3-}
\end{equation}

\begin{equation}
\text{Ni}_3\left[\text{Co}^{II}(\text{CN})_6\right]_2 + 9\text{OH}^- \rightarrow 3\text{Ni}^{II}\text{OOH} + 2\left[\text{Co}^{II}(\text{CN})_6\right]^{3-} + 3\text{H}_2\text{O} + 3\text{e}^-
\end{equation}

Furthermore, in the case of the core-shell PBA, the anodic reaction is complete after 10 min, while in the case of the single core PBA, the process takes considerably longer. Electron microscopy images (Figure S2, Supporting Information) indicate that the crystal core structure breaks-up in the process potentially loses electrical contact to the electrode and transformation is only through chemical etching. The rapid transformation of the core-shell structure PBA indicates that the amorphous shell prevents the break-up of the PBA core upon anodization and means the process is complete in 10 min.

Figure 6. The influence of anodic potential on the deprotonation of NiCo@A-NiCo-PBA-AA. a) XPS high-resolution spectra at Ni 2p edge of NiCo@A-NiCo-PBA-AA at applied voltages of 1.5, 1.55, and 1.6 V (vs RHE). The spectra were shown with raw data and fitting data derived by Lorentz–Gaussian function. b) The percentage content of different Ni species and the corresponding overpotentials at 50 mA cm$^{-2}$ of the samples under different anodization potential. c) The average Ni valence and the overpotentials at 50 mA cm$^{-2}$ of the samples under different activation voltage. d) Operando Raman spectra and the corresponding contour plot of NiCo@A-NiCo-PBA-AA obtained from the voltage increasing from 1.35 to 1.6 V (vs RHE). e) The proposed potential-dependent deprotonation reaction scheme of NiCo@A-NiCo-PBA-AA.
2.4. Active Site Identification

2.4.1. Proton Transfer Number Under the Influence of Anodic Potential

To further understand the influence of anodic potential on the number of proton transfer of Ni, the core-shell structure PBAs prepared under different anodic potentials were used for the OER test. It is observed the sample under anodization at 1.55 V versus RHE had the best OER activity (Figure S12, Supporting Information). XPS was performed for the analysis of the valence variation of Ni (Figure 6a). At a low anodization potential of 1.5 V, the Ni 2p$_{1/2}$ and 2p$_{3/2}$ spectrum of the core-shell PBA was fitted into three peaks at 856.9 and 858.5 eV, 863.6 and 874.3 eV, 875.8 and 881.5 eV, respectively, which corresponded to Ni$^{2+}$, Ni$^{3+}$, and satellite peak. When the initial NiCo@A-NiCo-PBA interacted with alkaline solution, hydrogen atoms were partially extracted from the hydroxyl group, and thus it is observed Ni$^{2+}$ and Ni$^{3+}$ coexisted in the system, and Ni$^{2+}$ dominates. When the voltage was raised to 1.55 V, further valence increases of nickel ions to Ni$^{3+}$/Ni$^{4+}$ states occurred by successive oxidation with associated deprotonation, which caused the formation of a partial intermediate NiOOH$_{1-x}$ species. When the voltage continued to reach 1.6 V, the high potential resulted in a local high concentration of Ni ions, thereby inhibiting the reducing ability of Ni, which led to the increase of Ni$^{4+}$ ratio, and the Ni$^{3+}$ in the sample being dominant. A potential-dependent deprotonation reaction scheme was proposed as Figure 6e.

Based on XPS (Figure 6a–c) and the OER tests (Figure S12, Supporting Information), the content of Ni species in the samples under different anodic potential and the overpotentials of the corresponding samples are shown in Figure 6b, and the average Ni valence was calculated to show the trend of OER activity with the degree of deprotonation, as shown in Figure 6c. It is concluded by increasing the anodic potential, the degree of deprotonation increases, and the activity of the corresponding sample first increases and then decreases. In order to further understand the intermediate products of the anodization process, operando Raman was performed and shown in Figure 6d. The results showed that as the anodization voltage increased from 1.35 to 1.6 V versus RHE, the characteristic peaks of Ni$^{2+}$ species gradually weakened, accompanied by the enhancement of the characteristic peak of Ni$^{3+}$/Ni$^{4+}$ species, which verified the conversion process from Ni$^{2+}$ to Ni$^{3+}$/Ni$^{4+}$. It is worth noting that under a voltage of 1.5 V, a strong peak appeared at 513 cm$^{-1}$, suggesting a combination of Ni$^{3+}$/Ni$^{4+}$ with adsorbed oxygen, corresponding to the oxidation peak in Figure 5b, this indicates the intermediate state of Ni$^{3+}$/Ni$^{4+}$−O$. Combining with the XPS results (Figure 6a–c) and the OER performance with the increase of anodized potential (Figure S12, Supporting Information), it is found the OER activity of the catalyst was greatly affected by the average valence state of Ni ions, and Ni$^{2+}$ was converted to Ni$^{3+}$ and Ni$^{4+}$ in NiOOH$_{1-x}$ with the increase in anodic voltage playing an important role during the OER catalysis, indicating that the Ni ions are the actual active sites.

![Figure 7. Interpretation of the relationship between Ni valence with OER activity. a) Projected density of states analysis of Ni metal atoms in the Ni(OH)$_2$, NiO$_2$H$_{1.5}$, NiO$_2$H$_2$, and NiO$_2$H$_{3.5}$ systems. The Fermi level is set as zero (inset: structural models of the NiO$_2$H$_x$ systems). b) Schematic mechanism of the OER activity change with the Ni valence ascending. c) The proposed scheme of OER mechanism for NiCo@A-NiCo-PBA-AA electrocatalyst.](image-url)
2.4.2. Interpretation of the Relationship Between Ni Valence with OER Activity

DFT was performed to further determine how the increase in the Ni valence affects the catalytic activity. It is well documented that the electrocatalytic activity is strongly dependent on the adsorption strength of reaction intermediates on a catalysts surface, which is further intimately related to the electronic structure of active sites.\textsuperscript{[53–57]} Therefore, the structural model (\textbf{Figure 7a}, inset) and density of states (DOS) (\textbf{Figure 7a}) of Ni atoms in the Ni(OH)\textsubscript{2}, NiO\textsubscript{2}H\textsubscript{1.5}, NiO\textsubscript{2}H\textsubscript{1}, and NiO\textsubscript{2}H\textsubscript{0.5} systems were simulated to track the evolution process of the geometric and electronic structures of Ni sites. It is shown that as the degree of deprotonation increases, the DOS of Ni atoms gradually shifts negatively, representing the loss of the electrons with high energy level for Ni\textsuperscript{2+} species, that is, an increase in the Ni oxidation state. More importantly, it is apparent that the DOS of the unoccupied atomic orbitals around the Fermi level of the Ni atoms gradually increases with the Ni oxidation state, which will lead to the continuous increase in the adsorption strength of oxygen-containing species in the OER process. According to the reported results,\textsuperscript{[33–35,58–61]} the catalytic activity of NiO\textsubscript{2}H\textsubscript{2–x} (0 ≤ x ≤ 2) systems exhibit a volcano relationship for the adsorption thermodynamics of intermediates. As depicted in \textbf{Figure 7b}, from Ni(OH)\textsubscript{2} to NiO\textsubscript{2}H\textsubscript{0.5}, the monotonic increasing in the adsorption strength of oxygen-containing species will cause the OER activity to cross the top of volcano, implying that the OER activity first rises and then falls as the Ni valence gradually increases, which agrees well with the experimental results. According to the results above, a OER mechanism of the

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure8.png}
\caption{Electrochemical analysis for hydrogen evolution reaction and water-splitting process. a) Polarization curves for NiCo@A-NiCo-PBA-AA and NiCo-PBA-AA in 1 m NaOH. b) Tafel plots of polarization curves of NiCo@A-NiCo-PBA-AA and NiCo-PBA-AA. c) Chronoamperometry measurement of NiCo@A-NiCo-PBA-AA at an anodic voltage 0.18 V (vs RHE). d) The Tafel slope comparison and the overpotential comparison needed to deliver cathodic current densities of 10, 50, and 100 mA cm\textsuperscript{-2} for NiCo@A-NiCo-PBA-AA and NiCo-PBA-AA in electrochemical HER. e) Electrolyte contact angles of NiCo@A-NiCo-PBA and NiCo-PBA before and after chronoamperometry measurement. f) Overall water-splitting performance of NiCo@A-NiCo-PBA-AA electrode couple in 1 m NaOH (Inset: Chronoamperometry test for NiCo@A-NiCo-PBA-AA at an anodic potential of 1.6 V in 1 m NaOH). g–i) Comparisons of OER, HER, and water-splitting catalytic activity with some recently reported nonprecious catalysts in alkaline electrolyte.}
\end{figure}
NiCo@A-NiCo-PBA-AA was proposed as follows, the schematic is shown in Figure 7c:

\[ \text{Ni}(OH)_2 + \text{OH}^- \rightarrow \text{NiOOH} + \text{H}_2\text{O} + e^- \]  

(3)

\[ \text{NiOOH} + \text{OH}^- \rightarrow \text{NiOO} + \text{H}_2\text{O} + e^- \]  

(4)

\[ \text{NiOO} + 2\text{OH}^- \rightarrow \text{Ni}(OH)_2 + \text{O}_2 + 2e^- \]  

(5)

**Summary**: \[ 4\text{OH}^- \rightarrow \text{O}_2 + 2\text{H}_2\text{O} + 4e^- \]  

(6)

### 2.5. Electrochemical Evaluation on Water Electrolysis Application

NiCo@A-NiCo-PBA-AA was also used for a HER test. As shown in Figure 8a,d and Table S1, Supporting Information, the as-prepared core-shell catalyst exhibits an onset potential of 37 mV, which is much less than the core PBA (178 mV). A relatively low overpotential of 173 mV was required for NiCo@A-NiCo-PBA-AA to offer a cathodic current density of 10 mA cm\(^{-2}\), which is much less than the core PBA (178 mV). In contrast, NiCo-PBA-AA required an overpotential of 292 mV. Moreover, the corresponding Tafel slope (Figure 8b,d) of the core-shell PBA (74.1 mV dec\(^{-1}\)) is smaller than that of the core PBA (104.3 mV dec\(^{-1}\)). Besides the good activity, excellent stability is also significant for energy conversion. Impressively, as illustrated in Figure 8c, the re-constructed NiCo@A-NiCo-PBA-AA showed excellent stability with no obvious performance degradation over 40 h. The high performance of the core-shell PBA is mainly because of the transformation to the partially amorphous Ni(OH)\(_2\) during anodic activation.

With all the advantages discussed above, NiCo@A-NiCo-PBA-AA was adopted as bifunctional electrodes in a water splitting electrolysis cell. Before the test, electrolyte contact angle measurement were carried out to indicate the wettability of the electrode (Figure 8e). The NiCo@A-NiCo-PBA-AA electrode displayed super-hydrophilic properties after anodic activation (contact angle: 22.40°), this indicates good contact of catalyst with the electrolyte. As illustrated in Figure 8f, the current density is 13.7 mA cm\(^{-2}\) at a cell voltage of 1.6 V, demonstrating the excellent catalytic activity of the as-prepared catalyst. In addition, there is no distinct attenuation under 40 h chronoamperometry operation (Figure 8f, inset). Above all, the OER, HER, and water-splitting activity of the low-cost PBA-based catalyst (NiCo@A-NiCo-PBA-AA) is comparable to that of most of the nonprecious metal materials (Figure 8g.h,i and Tables S3–S5, Supporting Information) and superior to PBA-derived materials (Tables S6–S8, Supporting Information) reported, showing great potential in the application of alkaline water electrolysis.

### 3. Conclusion

In summary, we demonstrate an approach to promoting transformation of an inactive but low-cost PBA and boosting its OER performance by constructing an amorphous homogenous shell on the surface of the core. The transformed core-shell PBA outperforms the transformed core PBA, with a more complete conversion to NiOOH. The core-shell PBA was used as a model to explore the origin and evolution of the OER activity at the atomic level. It is found that the partially amorphous nickel hydroxide after activation acts as an active species, and the wrapping of shell facilitates the transformation of PBA and protects the integrity of the materials. More importantly, the increased anodization potential leads to an increase in the Ni valence, resulting in an increase in the adsorption strength of oxygen-containing intermediates, demonstrating a volcano relationship with the OER activity.

Our work reveals the conversion path and indicates the underlying mechanism of the PBA-based framework in the water oxidation process. The transformation of PBA-based materials was well demonstrated and can be integrated with the OER mechanism of the existing oxides and perovskites to form a whole, new design strategy and catalytic mechanism for other MOF-based materials.

**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

Research data are not shared.

### Keywords

amorphous shell, deprotonation, electrocatalysis, Prussian blue analogues, transformation

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