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Hierarchical Spiked $\text{Co}_{0.85}\text{Se}$ Microcrystals on Nickel Foam as an Efficient Electrocatalyst for Urea Oxidation Reaction

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Abstract

We report the facile synthesis of hierarchical spiked cobalt selenide ($\text{Co}_{0.85}\text{Se}$) microcrystals grown on nickel foam (NF) via a hydrothermal method followed by selenization. Derived from cobalt hydroxyl fluoride ($\text{Co}(\text{OH})\text{F}$) microcrystals, the resulting $\text{Co}_{0.85}\text{Se}$ structures exhibit a robust architecture with well-defined spikes that offer abundant active sites and promote efficient charge transfer, thereby enhancing their electrocatalytic bifunctional activity toward the oxygen evolution reaction (OER) and urea oxidation reaction (UOR). The $\text{Co}_{0.85}\text{Se}/\text{NF}$ electrode delivers low overpotentials of 357 mV for OER and 236 mV for UOR at 100 mA cm^{-2} . Furthermore, it exhibits a small Tafel slope (34.3 mV dec^{-1}) and excellent durability for 24 h at 100 mA cm^{-2} during UOR. This simple and cost-effective strategy highlights the potential of hierarchical spiked $\text{Co}_{0.85}\text{Se}$ microcrystals as highly efficient electrocatalysts for urea-assisted OER and related sustainable energy conversion applications.

Keywords: $\text{Co}_{0.85}\text{Se}$ electrocatalyst; hydrothermal; spike-like microcrystals; urea-assisted oxygen evolution reaction

1. Introduction

The growing depletion of fossil fuels and the resulting environmental challenges have intensified the global pursuit of sustainable and clean energy technologies. Among various strategies, electrochemical water splitting is considered one of the most promising routes for hydrogen production [1–3]. However, its efficiency is significantly limited by the sluggish kinetics of the oxygen evolution reaction (OER) occurring at the anode [4,5]. A practical strategy to mitigate this issue involves replacing OER with the urea oxidation reaction (UOR), which proceeds at a much lower thermodynamic potential (0.37 V vs. 1.23 V for OER) [6–9]. Moreover, UOR not only reduces the overall energy input for hydrogen generation but also enables the electrochemical remediation of urea-rich wastewater. Therefore, the development of efficient, stable, and low-cost electrocatalysts for UOR is of great importance for both energy and environmental applications [10].

To date, a wide range of transition metal-based materials, particularly Ni-, Co-, and Fe-containing oxides, hydroxides, phosphides, and sulfides, have been explored as UOR electrocatalysts [11–16]. Among them, Ni-based catalysts dominate due to their ability to form high-valence $\text{Ni}^{3+}/\text{Ni}^{4+}$ species that act as the active centers during urea oxidation [17–19].



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Recent studies have shown that Ni-based materials, such as Ni(OH)₂/NiOOH, Ni-based alloys, and Ni chalcogenides, can achieve overpotentials typically in the range of 200–350 mV at current densities of 10–100 mA cm^{−2}, with Tafel slopes of 40–80 mV dec^{−1}, owing to the in situ formation of catalytically active NiOOH species under alkaline UOR conditions [17–19]. Despite their promising activity, Ni-based catalysts often suffer from limited intrinsic electrical conductivity and structural degradation at high current densities, motivating the exploration of alternative transition-metal-based systems. In this context, cobalt-based catalysts have attracted increasing attention because of their similar redox behavior and flexible electronic configuration, which can facilitate the adsorption and dehydrogenation of urea molecules [20–22].

In recent years, cobalt selenides have emerged as promising candidates for diverse electrochemical reactions, including OER, the hydrogen evolution reaction (HER), and overall water splitting [23–25]. Their high electrical conductivity, adjustable electronic structure, and stable surface chemistry enable fast charge transfer and excellent catalytic durability. Despite these advantages, studies on the application of cobalt selenides toward UOR remain limited. For example, Xu et al. prepared yolk-shell CoSe₂ for efficient urea electrolysis, achieving notable UOR performance [26]. Zhao et al. synthesized self-supported CoSe₂ nanorods that delivered an overpotential of 260 mV and a Tafel slope of 94.83 mV dec^{−1} [27]. Similarly, Lu et al. reported a CoSe₂ hollow cube/CoSe₂ nanosheet heterostructure that achieved 100 mA cm^{−2} at a low potential of 1.48 V (250 mV), saving 270 mV compared to OER [28]. Among cobalt selenide phases, non-stoichiometric Co_{0.85}Se is particularly attractive due to its intrinsic cobalt vacancies, which modulate the electronic structure, enhance electrical conductivity, and increase the density of unsaturated Co active sites compared with stoichiometric phases such as CoSe₂. These characteristics are highly beneficial for the UOR, where fast charge transfer and effective adsorption of urea-derived intermediates are required. In addition, Co_{0.85}Se readily undergoes surface reconstruction under alkaline anodic conditions to form catalytically active CoOOH species while preserving a conductive selenide framework. The defect-rich lattice also facilitates the formation of hierarchical architectures with high electrochemically active surface area, making Co_{0.85}Se a promising electrocatalyst for efficient and durable UOR.

Given these findings, a systematic investigation of cobalt selenide as a potential UOR electrocatalyst is essential to elucidate its intrinsic activity, stability, and surface reconstruction behavior under operating conditions. In this work, we synthesized spiked Co_{0.85}Se microcrystals directly grown on nickel foam (NF) via a facile hydrothermal-selenization approach and evaluated their bifunctional electrocatalytic performance toward OER and UOR in alkaline media. The precursor cobalt hydroxyl fluoride (Co(OH)F) served as a structural template to generate the spiked Co_{0.85}Se architecture. The resulting Co_{0.85}Se/NF electrode exhibited outstanding catalytic activity, requiring only 357 mV and 236 mV to achieve 100 mA cm^{−2} for OER and UOR, respectively, along with excellent durability over 24 h and a small Tafel slope (34.3 mV dec^{−1}). This study provides an effective strategy for constructing robust Co-based selenide architectures as efficient and durable electrocatalysts for urea-assisted water electrolysis and other sustainable energy applications.

2. Results and Discussion

The morphology of the Co(OH)F and Co_{0.85}Se electrodes was characterized by field-emission scanning electron microscopy (FESEM). As shown in Figure 1a–c, the Co(OH)F precursor consists of densely packed microcrystals with well-defined polyhedral shapes, primarily exhibiting smooth surfaces and sharp edges. The individual particles are about 1 μm in size and display compact, faceted geometries, indicating good crystallinity and mechanical robustness. Such a stable polyhedral framework provides a suitable template

for the subsequent selenization process. The corresponding energy-dispersive X-ray spectroscopy (EDS) spectrum (Figure S1a) confirms the presence of Co, O, and F elements in the Co(OH)F precursor.

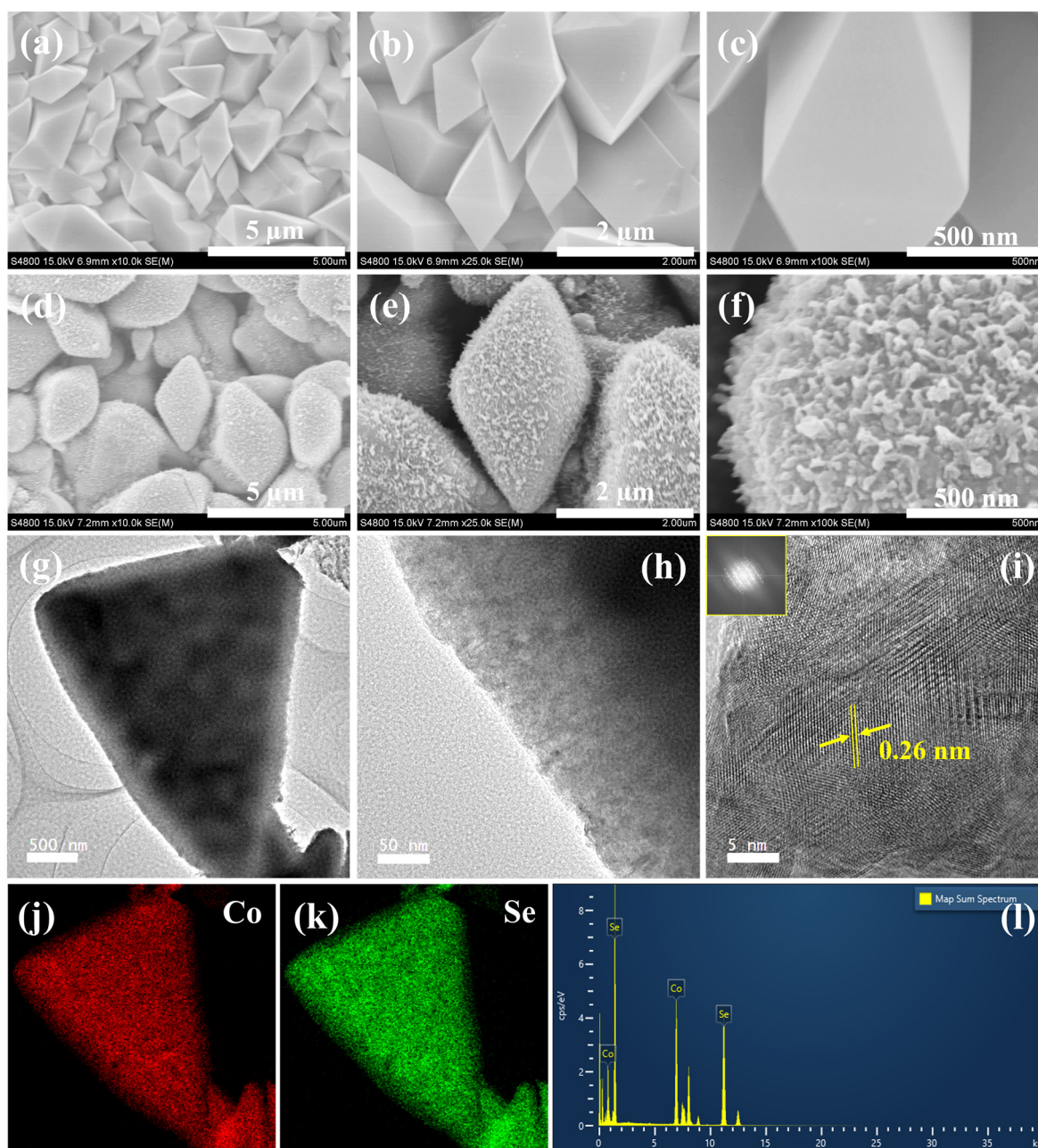


Figure 1. (a–c) FESEM images of Co(OH)F microcrystals. (d–f) FESEM images of Co_{0.85}Se microcrystals. (g–i) TEM and HRTEM images of Co_{0.85}Se microcrystals. (j,k) Elemental mapping of Co and Se. (l) Corresponding EDX spectrum.

After selenization, the Co(OH)F precursor is converted into Co_{0.85}Se microcrystals with a distinct hierarchical surface structure (Figure 1d–f). The overall polyhedral morphology is retained; however, the surfaces become densely decorated with fine, spike-like protrusions, resulting in a roughened texture. This transformation significantly enhances the surface area and exposes numerous electroactive sites, which are beneficial for facilitating the urea-assisted OER. Owing to the non-uniform distribution and varying dimensions of the spike-like surface features, precise quantification of individual protrusions is challenging. As observed from FESEM analysis (Figure 1d), the polyhedral Co_{0.85}Se microcrystals exhibit

typical overall sizes in the range of approximately 1–3 μm , confirming their micrometer-scale hierarchical architecture. The EDS spectrum of $\text{Co}_{0.85}\text{Se}$ (Figure S1b) confirms the presence of Co and Se, verifying successful selenization.

Field-emission transmission electron microscopy (FETEM) images (Figure 1g,h) further corroborate the FESEM observations, showing a clear contrast between the dense core and the roughened surface layer composed of nanoscale features. The high-resolution TEM image (Figure 1i) reveals distinct lattice fringes with an interplanar spacing of 0.26 nm, corresponding to the (101) plane of $\text{Co}_{0.85}\text{Se}$, confirming its crystalline nature [29,30]. The inset SAED pattern displays sharp diffraction spots, consistent with a well-defined crystal structure. Elemental mapping (Figure 1j,k) demonstrates the uniform distribution of Co and Se throughout the microcrystal, while the corresponding EDS spectrum (Figure 1l) shows Co and Se peaks, confirming the high purity of the synthesized $\text{Co}_{0.85}\text{Se}$ material, making it a promising electrocatalyst for urea-assisted OER.

Figure 2a shows the XRD patterns of the synthesized samples, confirming the formation of orthorhombic $\text{Co}(\text{OH})\text{F}$ (JCPDS No. 50-0827) [31,32] and its successful conversion into hexagonal $\text{Co}_{0.85}\text{Se}$ (JCPDS No. 52-1008) after the selenization treatment. The diffraction peaks located at 33.6° (101), 45.0° (102), 51.1° (110), 60.5° (103), 62.5° (112), and 70.2° (202) match well with the standard $\text{Co}_{0.85}\text{Se}$ phase [33,34], confirming its high crystallinity and phase purity without any detectable secondary phases.

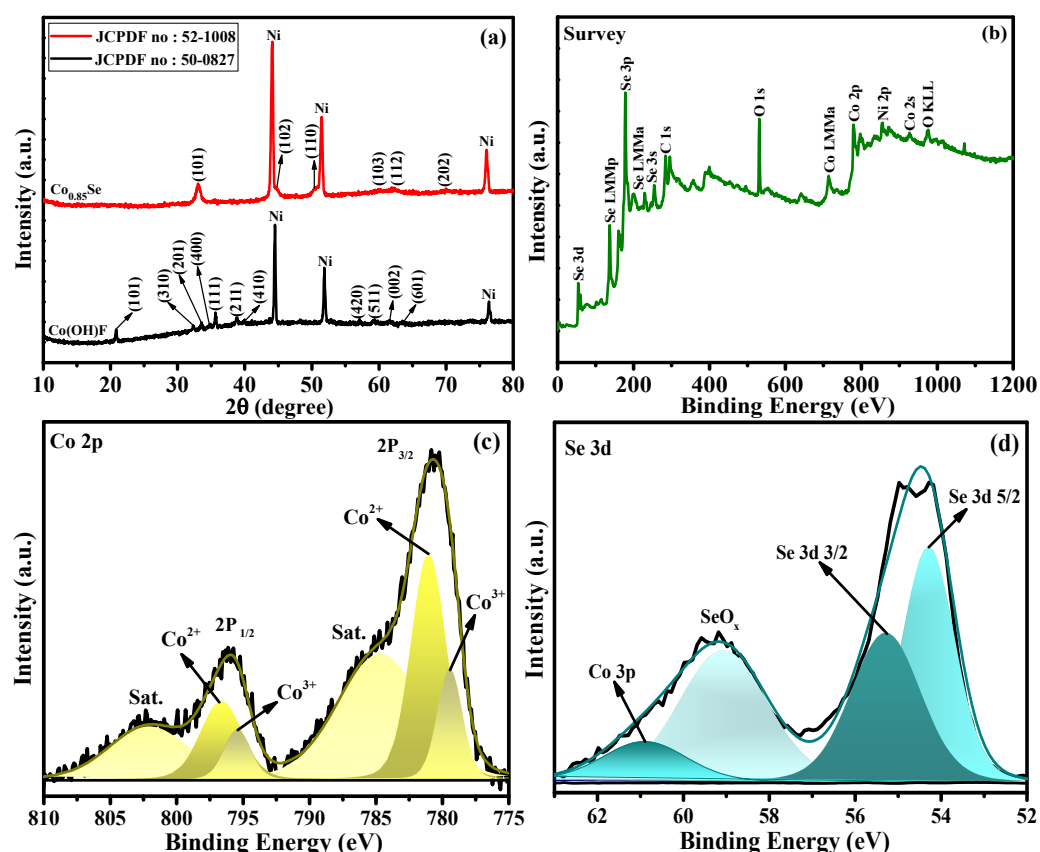


Figure 2. (a) XRD patterns of $\text{Co}_{0.85}\text{Se}/\text{NF}$ and $\text{Co}(\text{OH})\text{F}/\text{NF}$ electrocatalysts. (b) XPS survey spectrum of $\text{Co}_{0.85}\text{Se}$. (c) High-resolution Co 2p spectrum. (d) High-resolution Se 3d spectrum.

The surface chemical states of the $\text{Co}_{0.85}\text{Se}$ microcrystals were further examined using X-ray photoelectron spectroscopy (XPS). The survey scan (Figure 2b) reveals the presence of Co, Se, O, and C elements. The strong oxygen signals arise from Co–O, Se–O, and Co–O–Se bonding, while the weak carbon signals are related to atmospheric adventitious carbon. The high-resolution Co 2p spectrum (Figure 2c) displays two prominent peaks at

780.6 eV (Co 2p_{3/2}) and 796.1 eV (Co 2p_{1/2}), accompanied by well-defined satellite peaks at 785.1 eV and 802.2 eV [29,33,35]. These spectral features are characteristic of Co²⁺ and Co³⁺ species, confirming that cobalt exists in the +2 and +3 oxidation states. The Se 3d spectrum (Figure 2d) exhibits two main peaks centered at 54.3 eV (Se 3d_{5/2}) and 55.5 eV (Se 3d_{3/2}), corresponding to Se^{2−} species in metal selenides. The higher binding energy peak at 58.6 eV originates from oxidized Se–O species, indicating surface oxidation due to air exposure [36,37]. In addition to the Co 2p doublet, a subtle contribution from the Co 3p level is also observed in the lower binding energy region (around ~60 eV) [35]. Although the Co 3p signal is weak and often overlapped with Se–O related features, its presence supports the identification of cobalt in the selenide framework and further validates the Co–Se bonding environment. The coexistence of Se^{2−} and Se–O components suggest a mixed surface environment that may facilitate electron transfer processes relevant to UOR activity.

The electrocatalytic behavior of Co_{0.85}Se toward both the OER and UOR was systematically evaluated in alkaline electrolyte (1.0 M KOH with and without 0.33 M urea). Linear sweep voltammetry (LSV) curves recorded at a scan rate of 5 mV s^{−1} (Figure 3a) demonstrate a pronounced advantage for UOR compared with OER. For the OER, the small current feature observed around 1.35 V is attributed to the surface oxidation of cobalt species under alkaline conditions. In urea-containing electrolyte, this oxidation-related feature is not observed because the urea oxidation reaction is kinetically favored and dominates the anodic process at lower potentials, thereby suppressing or masking the surface oxidation current. To achieve a benchmark current density of 100 mA cm^{−2}, Co_{0.85}Se requires only 1.466 V (vs. RHE) for UOR, whereas 1.587 V is needed for OER, corresponding to a 121 mV reduction in overpotential. This substantial potential saving highlights both the lower thermodynamic barrier of urea oxidation and the superior catalytic activity of Co_{0.85}Se under operating conditions. Consequently, Co_{0.85}Se emerges as a promising anode material for energy-efficient electrolysis coupled with urea remediation.

Figure 3b presents statistical error-bar analysis comparing the anodic responses of OER and UOR, obtained from three independent measurements, and the error bars correspond to the standard deviation (±SD). For OER, the current density increases gradually with applied potential and rises sharply beyond ~1.50 V vs. RHE, indicating the onset of oxygen evolution. In contrast, UOR shows a markedly higher current response over the entire potential range, with an earlier and steeper increase. The small error bars for both reactions indicate excellent experimental reproducibility, while slightly larger deviations at higher potentials arise from intensified gas evolution and transient mass-transport effects. The superior UOR activity is attributed to the lower theoretical oxidation potential of urea (0.37 V vs. RHE) compared to water (1.23 V vs. RHE), enabling lower operating voltage and higher current output.

The catalytic performance of Co_{0.85}Se was further compared with its precursor Co(OH)F and the benchmark RuO₂ catalyst (Figure 3c). At a current density of 10 mA cm^{−2}, Co_{0.85}Se exhibits an overpotential of only 94 mV, which is significantly lower than that of Co(OH)F (149 mV) and RuO₂ (182 mV). The lower onset potential and higher current density over the entire potential range indicate that Co_{0.85}Se possesses favorable reaction thermodynamics and enhanced charge-transfer kinetics. The improved catalytic activity can be attributed to selenium incorporation, which modulates the electronic environment of cobalt and optimizes the adsorption energies of reaction intermediates. To evaluate the intrinsic contribution of the substrate, LSV curve of bare NF was performed under identical UOR conditions. As shown in Figure 3c, bare NF displays negligible urea oxidation activity compared with Co_{0.85}Se/NF, confirming that NF serves mainly as a conductive current collector and structural support, while the catalytic performance is dominated by the Co_{0.85}Se

active phase. Figure 3d presents statistical error bars obtained from three independent measurements for $\text{Co}_{0.85}\text{Se}$, $\text{Co}(\text{OH})\text{F}$, and RuO_2 . The current density values represent mean responses, while the error bars indicate the standard deviation ($\pm\text{SD}$). $\text{Co}_{0.85}\text{Se}$ exhibits a steady increase in current density with applied potential, followed by a pronounced rise beyond ~ 1.50 V vs. RHE, reflecting fast anodic reaction kinetics. $\text{Co}(\text{OH})\text{F}$ delivers higher current densities than RuO_2 across the entire potential range; for example, at 1.55 V vs. RHE, $\text{Co}(\text{OH})\text{F}$ reaches 58 mA cm^{-2} compared to 46 mA cm^{-2} for RuO_2 . The narrow error bars confirm excellent reproducibility and electrochemical stability, while slightly larger deviations at higher potential arise from intensified gas evolution and transient mass-transport effects.

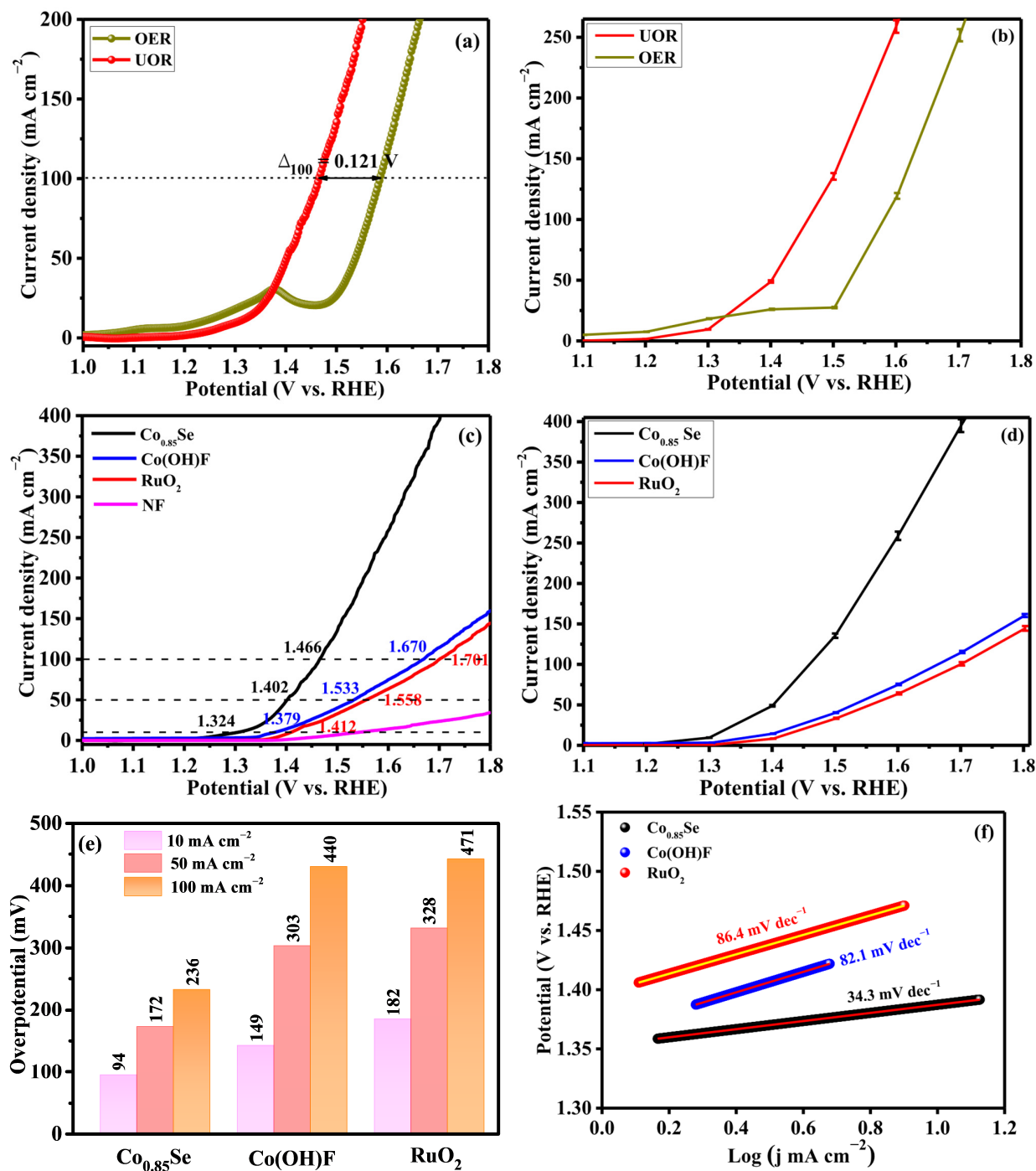


Figure 3. Cont.

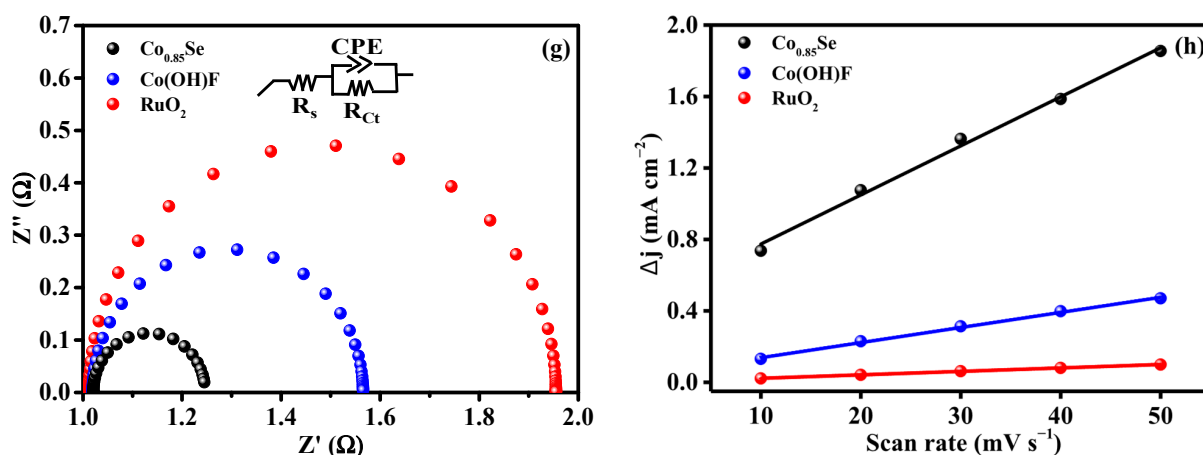


Figure 3. (a) LSV curves of $\text{Co}_{0.85}\text{Se}/\text{NF}$ in 1 M KOH and 1 M KOH + 0.33 M urea. (b) Error-bar polarization curves for OER and UOR in alkaline electrolyte (potential vs. RHE). (c) Comparison of UOR polarization curves for $\text{Co}_{0.85}\text{Se}$, Co(OH)F , RuO_2 , and NF electrocatalysts. (d) Error-bar polarization curves of $\text{Co}_{0.85}\text{Se}$, Co(OH)F , and RuO_2 under identical conditions. (e) Overpotentials at 10, 50 and 100 mA cm^{-2} for different catalysts. (f) Tafel plots. (g) Nyquist plots obtained from EIS. (h) Double-layer capacitance (C_{dl}) extracted from CV curves.

Furthermore, $\text{Co}_{0.85}\text{Se}$ requires the lowest potential to reach current densities of 50 and 100 mA cm^{-2} for UOR compared with Co(OH)F and RuO_2 (Figure 3e). The performance of $\text{Co}_{0.85}\text{Se}$ is also comparable to or even superior to that of many reported Co-based catalysts, such as yolk-shell CoSe_2 (160 mV at 50 mA cm^{-2}) [26], CoSe_2/Co nanorods (260 mV at 10 mA cm^{-2}) [27], CoSe_2 hollow cube/ CoSe_2 nanosheets (250 mV at 100 mA cm^{-2}) [28], and $\text{Co}/\text{CoSe}_2@\text{CN}_x$ (140 mV at 10 mA cm^{-2}) [38] (Table 1). To visually highlight the superior UOR performance, a bar chart comparing the overpotential at 10 mA cm^{-2} (η_{10}) of $\text{Co}_{0.85}\text{Se}$ with representative catalysts from the literature is presented in Figure S2.

Further insight into the intrinsic reaction kinetics was obtained from the Tafel analysis. $\text{Co}_{0.85}\text{Se}$ exhibits a Tafel slope of 34.3 mV dec^{-1} , which is significantly smaller than those of Co(OH)F (82.1 mV dec^{-1}) and RuO_2 (86.4 mV dec^{-1}) (Figure 3f). The reduced slope indicates faster charge-transfer kinetics and a more favorable reaction pathway. A Tafel slope in the range of 30–50 mV dec^{-1} suggests a mechanism involving a rapid pre-equilibrium step followed by a rate-determining electron-transfer or chemical step. Accordingly, $\text{Co}_{0.85}\text{Se}$ sustains high current densities with smaller incremental energy input, a desirable characteristic for practical electrolyzer operation. The $\text{Co}_{0.85}\text{Se}$ catalyst exhibits an exceptionally low Tafel slope of 34.3 mV dec^{-1} for the urea oxidation reaction, indicating a distinct kinetic regime dominated by a fast electrochemical step rather than interfacial charge-transfer limitations. In alkaline media, UOR proceeds through urea adsorption, sequential dehydrogenation of $-\text{NH}_2$ groups, C–N bond cleavage, and oxidation of carbon-containing intermediates to carbonate species. The low Tafel slope suggests that urea adsorption and $^*\text{CO}$ oxidation are not rate-determining on $\text{Co}_{0.85}\text{Se}$. Instead, the kinetics are consistent with a rate-determining dehydrogenation step of adsorbed urea-derived intermediates (e.g., $^*\text{NH}_2 \rightarrow ^*\text{NH}$), which involves a relatively low activation barrier. The incorporation of Se plays a critical role in modulating the electronic structure of Co active sites. Owing to its larger atomic radius and lower electronegativity, Se induces electron redistribution around Co centers and shifts the Co d-band center closer to the Fermi level, thereby optimizing the adsorption energies of key nitrogen-containing intermediates ($^*\text{NH}_2$ and $^*\text{NH}$). This electronic tuning facilitates urea dehydrogenation, reduces the energy barrier of the rate-determining step, and results in accelerated UOR kinetics with a markedly reduced Tafel slope. These results indicate that the enhanced

catalytic performance arises from intrinsic electronic structure modulation rather than solely from improved charge-transfer properties.

Table 1. Comparison of UOR performance for Co_{0.85}Se microcrystals with other selenide-based materials [39–45].

Electrocatalysts	Overpotential (mV)	Tafel Slope (mV dec ^{−1})	Electrolyte	Ref.
Co _{0.85} Se/NF	$\eta_{10} = 94$ $\eta_{50} = 172$ $\eta_{100} = 236$	34.3	1 M KOH + 0.33 M urea	This work
Yolk-shell CoSe ₂	$\eta_{50} = 160$	69.8	1 M KOH + 0.5 M urea	[26]
CoSe ₂ nanorods	$\eta_{10} = 260$	94.83	1 M KOH + 1 M urea	[27]
CoSe ₂ hollow cube/CoSe ₂ nanosheets	$\eta_{100} = 250$	44.5	1 M KOH + 0.5 M urea	[28]
Co/CoSe ₂ @CN _x	$\eta_{10} = 140$	-	1 M KOH + 0.33 M urea	[38]
2D CoSe ₂ /Ni _{0.85} Se	$\eta_{100} = 100$	26.0	1 M KOH + 0.5 M urea	[39]
Ni ₂ P/CoSe ₂	$\eta_{100} = 153$	42.0	1 M KOH + 0.5 M urea	[40]
Ni _{0.85} Se/CoSe ₂	$\eta_{10} = 62$	86.3	1 M KOH + 0.33 M urea	[41]
NiCoSe MS nanospheres	$\eta_{10} = 62$	29.1	1 M KOH + 0.33 M urea	[42]
Ni-CoMn _{0.3} Se ₂ /NF-5	$\eta_{100} = 165$	40.0	1 M KOH + 0.5 M urea	[43]
Mo-Co ₉ Se ₈ /Fe-NiSe/Ni ₃ Se ₂ /NF	$\eta_{10} = 172$	44.0	1 M KOH + 0.5 M urea	[44]
V-NiSe/FeSe/FNSe/NF	$\eta_{10} = 80$	29.42	1 M KOH + 0.5 M urea	[45]

Electrochemical impedance spectroscopy (EIS) measurements (Figure 3g) further corroborate the kinetic advantages of Co_{0.85}Se. The EIS spectra were recorded at 1.330 V (vs. RHE), and the impedance data were fitted using the equivalent circuit model shown in the inset. The Nyquist plots reveal a much smaller semicircle diameter for Co_{0.85}Se than for Co(OH)F and RuO₂, indicating a lower charge-transfer resistance (R_{ct}). The R_{ct} value of Co_{0.85}Se (22 Ω) is significantly lower than that of Co(OH)F (58 Ω) and RuO₂ (65 Ω). The reduced R_{ct} demonstrates improved electrical conductivity and faster interfacial electron exchange between the catalyst surface and reactive intermediates. Such behavior is consistent with the metallic or semi-metallic nature of the Co–Se bonding network, which facilitates more efficient charge transport compared with hydroxide or oxyfluoride phases, thus supporting the superior LSV and Tafel results.

The electrochemical double-layer capacitance (C_{dl}) was estimated from non-Faradaic current–scan rate relationships (Figure 3h). Cyclic voltammetry (CV) measurements were conducted at different scan rates, and the corresponding CV curves are shown in Figure S3. Co_{0.85}Se exhibits a substantially larger C_{dl} (44.1 mF cm^{−2}) than Co(OH)F (2.44 mF cm^{−2}) and RuO₂ (13.9 mF cm^{−2}), indicating a significantly increased ECSA. This enhancement is attributed to the surface roughening and structural reconstruction induced during the selenization process, which expose more catalytically active sites. The synergy between the enlarged active surface area and the improved intrinsic site activity arising from Se incorporation collectively accounts for the superior UOR performance of Co_{0.85}Se.

Long-term stability is a key requirement for the practical application of UOR electrocatalysts. The durability of the Co_{0.85}Se electrode was evaluated by chronopotentiometry at a constant current density of 100 mA cm^{−2} for 24 h. As shown in Figure 4a, the potential of Co_{0.85}Se remains nearly unchanged throughout the entire test period, demonstrating excellent operational stability. Moreover, the LSV curve recorded after the stability test closely overlaps with the initial one (Figure 4c), confirming the remarkable electrochemical

durability of $\text{Co}_{0.85}\text{Se}$ under continuous anodic operation. For comparison, the stability of the $\text{Co}(\text{OH})\text{F}$ electrode was also tested at 100 mA cm^{-2} for 24 h under identical conditions (Figure 4a). Unlike $\text{Co}_{0.85}\text{Se}$, the polarization curve of $\text{Co}(\text{OH})\text{F}$ exhibited a noticeable shift after the long-term test (Figure 4b), indicating structural or compositional changes that lead to performance degradation. This comparison further highlights the superior durability of $\text{Co}_{0.85}\text{Se}$ as a UOR electrocatalyst. This outstanding stability can be attributed to two main factors: (i) the strong Co–Se bonding that suppresses catalyst dissolution and lattice distortion, and (ii) the in situ formation of a thin, stable CoOOH surface layer during anodic polarization, which preserves catalytic activity and protects the underlying structure from degradation. These synergistic effects ensure both the chemical and structural robustness of $\text{Co}_{0.85}\text{Se}$ under harsh electrolysis conditions.

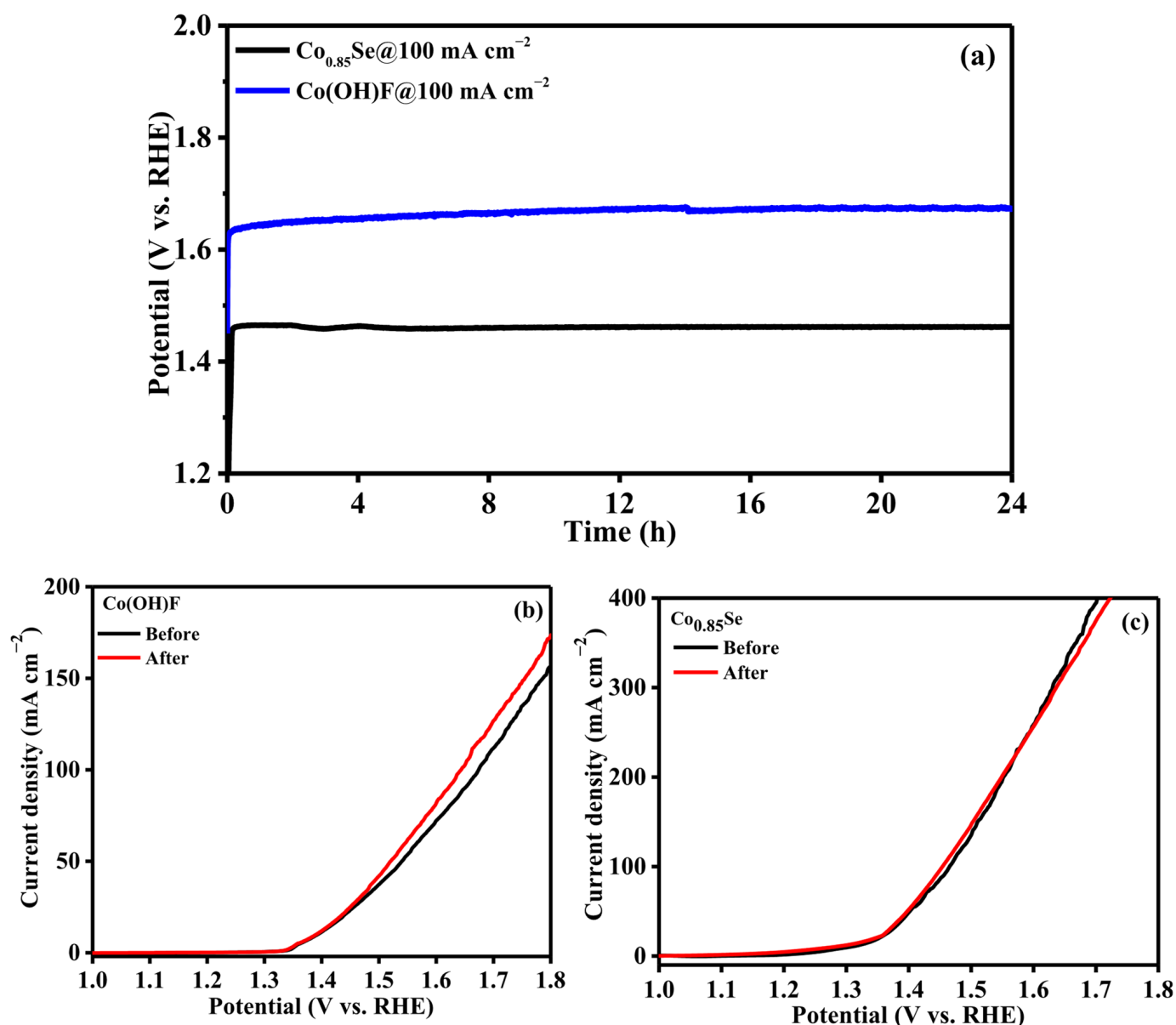


Figure 4. (a) Chronopotentiometry stability test of $\text{Co}_{0.85}\text{Se}/\text{NF}$ and $\text{Co}(\text{OH})\text{F}/\text{NF}$ at 100 mA cm^{-2} for 24 h. (b,c) LSV curves recorded before and after CP.

The surface morphology of the $\text{Co}_{0.85}\text{Se}/\text{NF}$ electrode before and after the long-term UOR stability test was examined by FESEM, as shown in Figures S4 and 5. Before electrolysis (Figure S4a,b), the $\text{Co}_{0.85}\text{Se}$ electrode exhibits densely packed polyhedral microcrystals

with roughened surfaces covered by fine nanoscale protrusions. This hierarchical surface texture, originating from the selenization of the Co(OH)F precursor, provides abundant active sites and efficient electrolyte accessibility. After 24 h of UOR operation at 100 mA cm^{-2} , the overall polyhedral morphology remains largely preserved (Figure S4c,d), indicating excellent structural robustness. However, the microcrystals display slightly coarsened surfaces with partial aggregation of nanoscale features (Figure 5a–c), reflecting mild surface reconstruction during prolonged electrolysis. The corresponding EDX spectrum (Figure 5e) confirms the presence of Co, Se, Ni, O, and minor C and K elements. The increased oxygen signal after the stability test suggests the formation of a surface CoOOH layer while the detectable Se signal indicates retention of the underlying Co–Se framework. These observations collectively demonstrate that Co_{0.85}Se maintains its microcrystalline architecture and chemical integrity, accounting for its excellent long-term stability and durability during urea oxidation.

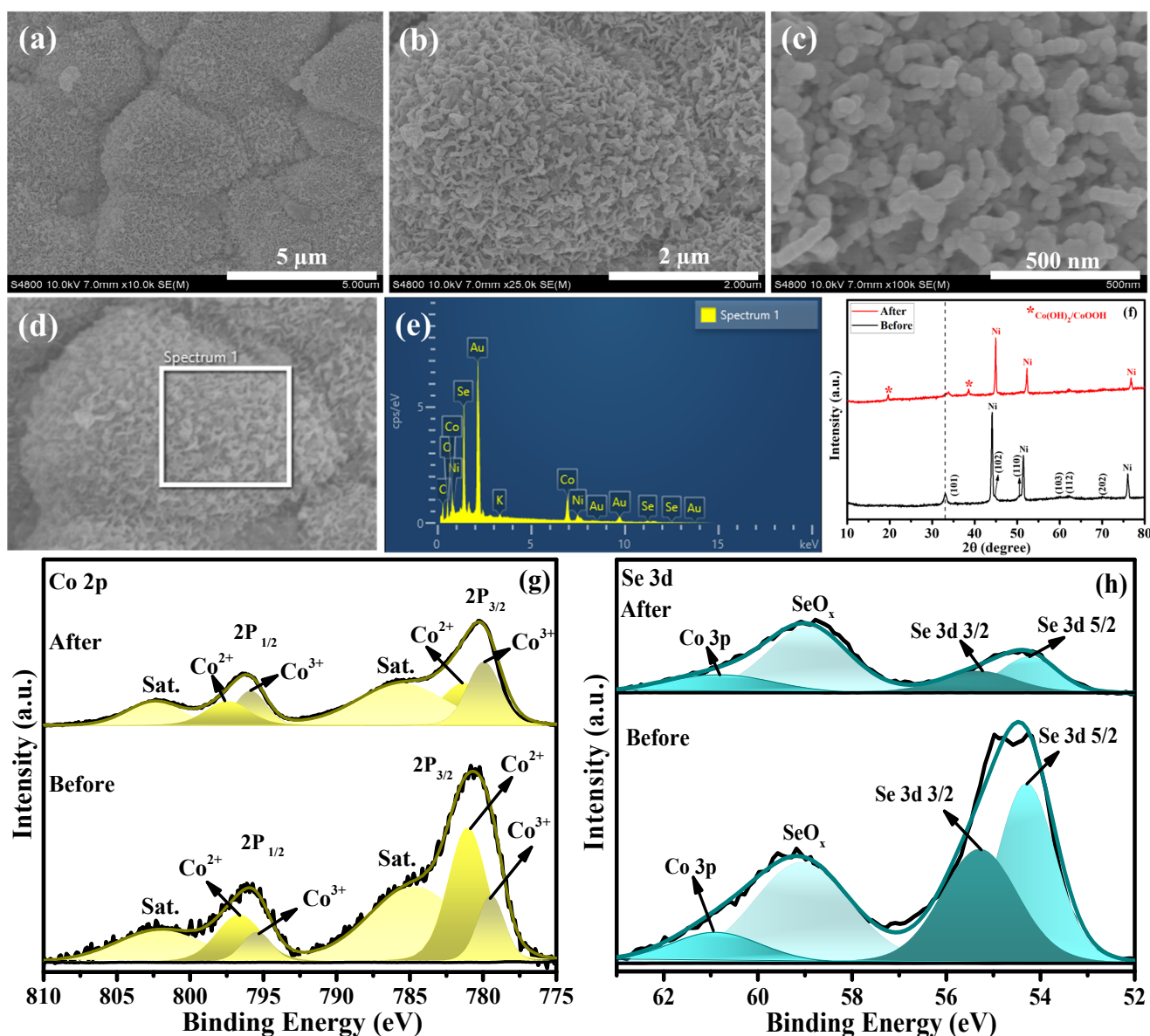
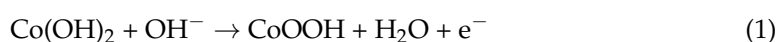


Figure 5. (a–d) FESEM images of Co_{0.85}Se/NF electrocatalyst after the CP stability test. (e) Corresponding EDX spectrum. (f) XRD patterns of Co_{0.85}Se/NF electrocatalysts before and after the UOR. (g) Deconvoluted Co 2p spectra before and after UOR. (h) Deconvoluted Se 3d spectra before and after UOR.

The crystalline phase of the Co_{0.85}Se/NF electrocatalyst after the UOR stability test was examined by XRD (Figure 5f). After the UOR stability test, the XRD pattern of Co_{0.85}Se/NF largely preserves the characteristic diffraction peaks of the Co_{0.85}Se phase, confirming the structural stability of the bulk selenide framework. Notably, two additional sharp peaks appear at approximately 19.5° and 38.5°, along with slight distortion of the main diffraction peak near 33°. These features are attributed to the formation of surface cobalt hydroxide/oxyhydroxide (Co(OH)₂/CoOOH) species induced by anodic oxidation under alkaline UOR conditions. Such surface reconstruction, while retaining a conductive selenide core, is commonly observed for cobalt chalcogenide electrocatalysts and is considered beneficial for sustained catalytic activity.

The excellent catalytic activity of Co_{0.85}Se toward UOR can be understood from the XPS analysis. The XPS spectra recorded before and after UOR clearly reveal the electron-transfer processes occurring in Co_{0.85}Se. After UOR, the Co 2p spectrum (Figure 5g) displays two main peaks at binding energies of 780.3 and 795.2 eV ± 0.1 eV, corresponding to the Co 2p_{3/2} and Co 2p_{1/2} spin-orbit components. These peaks can be deconvoluted into sub-peaks at 779.9 and 796.2 eV, which represent Co³⁺ species and confirm the effective oxidation of Co²⁺ to Co³⁺ compared with the pre-UOR state. In addition, the peaks appearing at 781.8 and 796.9 eV ± 0.5 eV are assigned to Co²⁺, indicating the coexistence of mixed oxidation states. For Se 3d, the spectra obtained before and after UOR (Figure 5h) show characteristic peaks at 54.2 and 56.2 eV, corresponding to Se 3d_{5/2} and Se 3d_{3/2}, along with a typical SeO_x feature at 58.89 eV. The preservation of the main Se^{2−} peaks, along with the observable oxide peak, indicates partial surface oxidation with an overlap of Co 3p further confirms the formation Co–Se framework.

Post-stability XPS analysis (Figure 5g,h) reveals a pronounced increase in the Co³⁺ component after prolonged urea oxidation, indicating surface reconstruction of Co_{0.85}Se under anodic polarization. During electrochemical urea oxidation in alkaline media, the catalyst surface undergoes in situ oxidation under anodic bias, generating high-valent metal oxyhydroxide surface phases (Co³⁺ in CoOOH). These high-valent species are widely recognized as electrocatalytically active centers for both OER and UOR due to their ability to facilitate multi-electron and proton transfer processes, as confirmed by the XPS analysis [46]. Mechanistically, the formation of Co³⁺ occurs through the electro-oxidation of lower-valent cobalt (Co²⁺) under applied positive potentials:



Surface reconstruction leads to the formation of an oxyhydroxide layer on Co_{0.85}Se. Once Co³⁺/CoOOH species are present on the surface, the adsorption and activation of urea (NH₂–CO–NH₂) can be rationalized in the context of electrochemical–chemical steps. Urea molecules coordinate more strongly to high-valent Co³⁺ active sites than to metallic or low-valent cobalt species because Co³⁺ exhibits a higher affinity for polar moieties, such as C=O and N–H donor/acceptor groups [47]. This enhanced adsorption orients the urea molecule such that the carbonyl carbon and adjacent NH₂ groups are favorably positioned for facile deprotonation and C–N bond activation, which is often the rate-determining step in UOR [8].

Following adsorption on Co³⁺ sites, Co³⁺ acts as an electron acceptor, while the urea molecule undergoes dehydrogenation through the loss of protons from its N–H groups and electrons to the external circuit. The high-valent Co³⁺ species facilitate this process by enabling efficient electron transfer and stabilizing partially dehydrogenated intermediates (e.g., *CONH₂ and *NH species). Similar behavior has been reported for NiOOH systems, in which Ni³⁺–O species interact with adsorbed urea and facilitate its oxidation to CO₂ and N₂, while Ni³⁺ is transiently reduced to Ni²⁺ during the reaction cycle [48].

In addition, the presence of Se^{2-} in the cobalt selenide lattice plays a synergistic role in stabilizing high-valence cobalt species and modulating the electronic structure of the catalyst. Selenium, having a lower electronegativity than oxygen, donates electron density to cobalt, thereby facilitating the reversible $\text{Co}^{2+}/\text{Co}^{3+}$ redox transition under anodic polarization. This electronic interaction lowers the energy barrier for Co^{3+} formation and enhances charge-transfer kinetics, which is consistent with the low Tafel slope observed for the $\text{Co}_{0.85}\text{Se}$ catalyst [49]. Furthermore, partial surface oxidation of Co–Se bonds during UOR likely generates Co–Se–O interfacial sites, which have been proposed as highly active motifs for urea adsorption and oxidation.

Based on these observations, a plausible UOR mechanism on $\text{Co}_{0.85}\text{Se}$ is proposed, as illustrated in Figure 6: (i) electrochemical oxidation of surface Co^{2+} to Co^{3+} to generate active sites; (ii) urea adsorption on Co^{3+} centers; (iii) Co^{3+} -mediated dehydrogenation and C–N bond cleavage assisted by OH^- ; and (iv) reduction of Co^{3+} back to Co^{2+} , completing the redox cycle [11]. The increased Co^{3+} content observed in the post-stability XPS spectra therefore provides direct spectroscopic evidence that high-valence cobalt species are not only stable under UOR conditions but also play a decisive role in sustaining high catalytic activity.

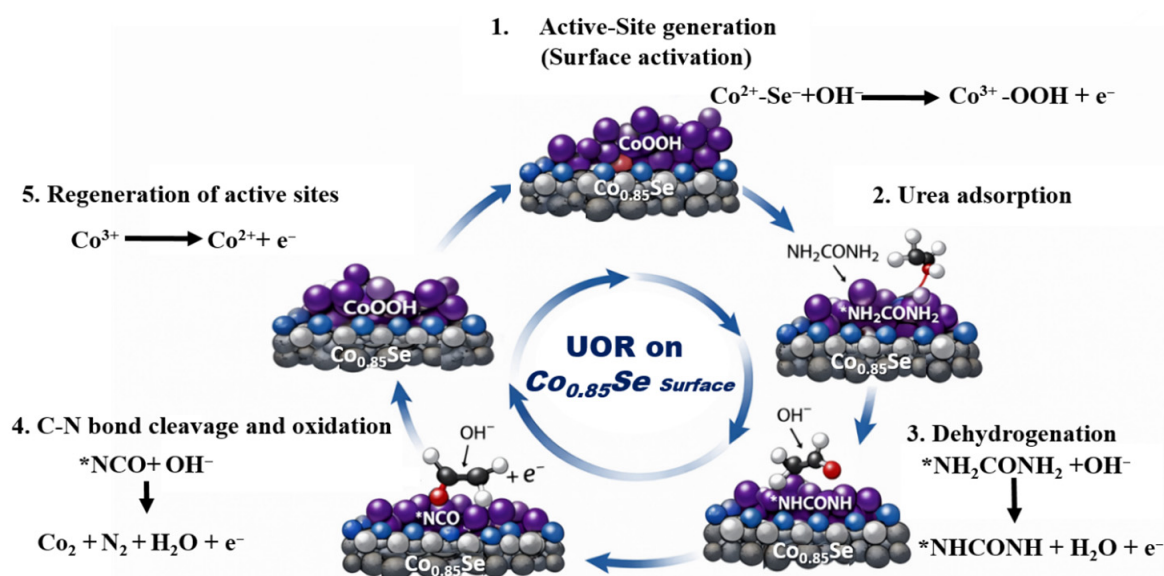


Figure 6. Schematic illustration of the UOR mechanism on the $\text{Co}_{0.85}\text{Se}$ surface.

Overall, the effective redox transitions of Co and Se reveal the electron-transfer processes involved during UOR. Co is predominantly oxidized from Co^{2+} to Co^{3+} , whereas Se 3d accepts electron density to maintain strong Co– Se^{2-} bonding. This synergistic electronic interaction enhances electrocatalytic activity by facilitating charge transfer and reducing the UOR overpotential.

3. Experimental Section

3.1. Materials

Cobalt nitrate hexahydrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), ammonium fluoride (NH_4F), sodium selenite (Na_2SeO_3), hydrazine hydrate ($\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$), urea, and potassium hydroxide (KOH) were purchased from Sigma-Aldrich. The RuO_2 benchmark catalyst used in this study was a commercially available material (Ruthenium (IV) oxide, 99.9% trace metals basis, Alfa Aesar). Ethanol ($\text{C}_2\text{H}_6\text{O}$) and deionized water (DI H_2O) were used as solvents, and NF substrates were obtained from MTI Corporation. All chemicals were of analytical grade and used without further purification.

3.2. Synthesis of Co(OH)F/NF Precursor

For the growth of the Co(OH)F nanostructure, 50 mM Co(NO₃)₂·6H₂O and 150 mM NH₄F were dissolved in 20 mL of DI H₂O under magnetic stirring for 10 min. The homogeneous solution was transferred to a 100 mL Teflon-lined stainless-steel autoclave containing a pre-cleaned NF substrate (10 mm × 50 mm) fully immersed in the reaction solution. The hydrothermal reaction was conducted at 120 °C for 12 h. After cooling to room temperature, the obtained Co(OH)F/NF precursor was thoroughly rinsed with DI H₂O and ethanol and then dried at 70 °C overnight.

3.3. Synthesis of Co_{0.85}Se/NF

The conversion of Co(OH)F to Co_{0.85}Se was achieved through a low-temperature selenization process. In a typical synthesis, 0.1 g of Na₂SeO₃ and 1 mL of hydrazine hydrate were dissolved in 20 mL DI H₂O under stirring for 10 min. The prepared Co(OH)F/NF precursor was then immersed into the solution and maintained at 120 °C for 6 h in a Teflon-lined autoclave. During this process, Se^{2−} species generated in situ from Na₂SeO₃ and hydrazine gradually replaced the F[−] ions, leading to the formation of spiked Co_{0.85}Se structures on the NF substrate. The resulting black product was collected, washed repeatedly with DI H₂O and ethanol, and dried at 70 °C for 12 h to obtain the final Co_{0.85}Se/NF electrode.

The morphology of Co_{0.85}Se is closely related to the synthesis conditions of the Co(OH)F precursor. Our previous study demonstrated that an optimized cobalt precursor concentration yields polyhedral Co(OH)F microcrystals with superior electrochemical properties [32]. Using this established condition, Co(OH)F templates were obtained in the present work and subsequently converted into hierarchical spiked Co_{0.85}Se during selenization, leading to enhanced UOR activity.

In this process, hydrazine hydrate serves as a reducing agent, converting SeO₃^{2−} ions from Na₂SeO₃ into reactive Se^{2−} species under hydrothermal conditions. The in situ-generated Se^{2−} ions subsequently replace F[−]/OH[−] species in the Co(OH)F precursor through an anion-exchange reaction, leading to the formation of hierarchical spiked Co_{0.85}Se microcrystals on the NF substrate.

Detailed characterization parameters and electrochemical testing procedures are provided in the Supplementary Information.

4. Conclusions

In summary, hierarchical spiked polyhedral Co_{0.85}Se microcrystals were successfully synthesized directly on NF via a facile hydrothermal method followed by selenization. The resulting Co_{0.85}Se/NF electrode exhibits outstanding UOR activity, delivering low overpotentials of 94 mV at 10 mA cm^{−2} and 236 mV at 100 mA cm^{−2}, along with a small Tafel slope of 34.3 mV dec^{−1} and excellent operational stability over 24 h in alkaline media. The superior UOR performance is attributed to the defect-rich Co_{0.85}Se phase, hierarchical spike-like morphology, and efficient electron transport enabled by the conductive NF substrate. From a practical perspective, the synthesis approach is amenable to scale-up, as it employs low-temperature, solution-based processing with commercially available precursors. The direct growth of Co_{0.85}Se on NF enables binder-free electrode fabrication and straightforward integration into urea electrolysis systems. Together with its high activity at industrially relevant current densities and excellent durability, the Co_{0.85}Se/NF electrode shows strong potential for large-scale urea-assisted hydrogen production and wastewater remediation.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/catal16030232/s1>, Experimental parts such as, materials characterization and

electrochemical measurements. Figure S1: (a,b) EDX spectra of Co(OH)F and Co_{0.85}Se microcrystals, respectively; Figure S2: Comparison of η_{10} values for Co_{0.85}Se/NF and representative cobalt-selenide UOR electrocatalysts in alkaline media; Figure S3: Typical CV curves recorded at different scan rates in the non-Faradaic region for (a) Co_{0.85}Se, (b) Co(OH)F, and (c) RuO₂ electrocatalysts; Figure S4: (a,b) FESEM images of as-prepared Co_{0.85}Se electrocatalyst. (c,d) FESEM images of Co_{0.85}Se electrocatalyst after CP stability study.

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