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#### Article

# Inception of Co<sub>3</sub>O<sub>4</sub> as Microstructural Support to Promote Alkaline Oxygen Evolution Reaction for Co<sub>0.85</sub>Se/Co<sub>9</sub>Se<sub>8</sub> Network

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ABSTRACT: Developing electrocatalysts with abundant active sites is a substantial challenge to reduce the overpotential requirement for the alkaline oxygen evolution reaction (OER). In this work, we have aimed to improve the catalytic activity of cobalt selenides by growing them over the self-supported  $Co_3O_4$  microrods. Initially,  $Co_3O_4$  microrods were synthesized through annealing of an as-prepared cobalt oxalate precursor. The subsequent selenization of  $Co_3O_4$  resulted in the formation of a grainy rodlike  $Co_3O_4/Co_{0.85}Se/Co_9Se_8$  network. The structural and morphological analysis reveals the presence of  $Co_3O_4$  even after the selenization treatment where the cobalt selenide nanograins are randomly covered over the  $Co_3O_4$  support. The resultant electrode shows superior electrocatalytic activity toward OER in alkaline medium by delivering a benchmark current density of 10 mA/cm<sup>2</sup><sub>geo</sub> at an overpotential of 330 mV. As a comparison, we have developed Co<sub>0.85</sub>Se/Co<sub>9</sub>Se<sub>8</sub> under similar conditions and evaluated its OER activity. This material consumes an overpotential of 360 mV to deliver the benchmark current density, which signifies the role of the  $Co_3O_4$  support to improve the electrocatalytic activity of  $Co_{0.85}Se/Co_9Se_8$ . Despite having a low TOF value for  $Co_3O_4/Co_{0.85}Se/Co_9Se_8$ .  $Co_9Se_8$  (0.0076 s<sup>-1</sup>) compared to  $Co_{0.85}Se/Co_9Se_8$  (0.0102 s<sup>-1</sup>), the improved catalytic activity of  $Co_3O_4/Co_{0.85}Se/Co_9Se_8$  is attributed to the presence of a higher number of active sites rather than the improved per site activity. This is further supported from the  $C_{dl}$  (double layer capacitance) measurements where  $Co_3O_4/Co_{0.85}Se/Co_9Se_8$  and  $Co_{0.85}Se/Co_9Se_8$  tender  $C_{dl}$  values of about 8.19 and 1.08 mF/cm<sup>2</sup>, respectively, after electrochemical precondition. As-prepared Co<sub>3</sub>O<sub>4</sub>/Co<sub>0.85</sub>Se/Co<sub>9</sub>Se<sub>8</sub> also manifests rapid kinetics (low Tafel slope ~ 91 mV/dec), long-term stability, low charge-transfer resistance, and 82% Faradaic efficiency for alkaline electrocatalysis (pH = 14). Furthermore, the proton reaction order ( $\rho$ RHE) is found to be 0.65, indicating a proton decoupled electron transfer (PDET) mechanism for alkaline OER. Thus, the  $Co_3O_4$  support helps in the exposure of more catalytic sites of  $Co_{0.85}$ Se/Co<sub>9</sub>Se<sub>8</sub> to deliver the improved catalytic activities in alkaline medium.

# **1. INTRODUCTION**

The day-to-day requirement of clean energy has been outraised with the green revolution. Consumption of fossil fuel dispels toxic compounds that limits their real-world execution for a sustainable system.<sup>1</sup> To date, hydrogen is in a commanding position due to carbon-free emission and high-energy output. In general, water electrolysis is one of the most convenient routes for hydrogen production. However, the complex pathway of the four-electron mechanism demands serious overpotentials for the electrochemical oxygen evolution reaction (OER).<sup>2</sup> In this regard, IrO<sub>2</sub> and RuO<sub>2</sub> are still considered as state-of-the art catalysts in acidic and alkaline mediums, respectively. High market price and scarceness hinder their industrial implementation for commercial practice.<sup>3,4</sup> Nonprecious cobalt-containing electrocatalysts

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Figure 1. (a) PXRD patterns of as-prepared samples of (i)  $Co_3O_4$  (sample S2), (ii)  $Co_3O_4/Co_{0.85}Se/Co_9Se_8$  (sample S4), and (iii)  $Co_{0.85}Se/Co_9Se_8$  (sample S5) along with standard pattern of  $Co_3O_4$  (JCPDS File # 43-1003),  $Co_9Se_8$  (JCPDS File # 01-089-4180), and  $Co_{0.85}Se$  (JCPDS File # 52-1008). XPS patterns of as-prepared  $Co_3O_4/Co_{0.85}Se/Co_9Se_8$  (sample S4) with narrow scan (b) C 1s, (c) Co 2p, (d) Se 3d, and (e) O 1s.

have been evolved as splendid candidates for alkaline OER because of their high abundance, low price, and elite redox property.<sup>5,6</sup> In recent times, extensive efforts have been devoted to designing cobalt-containing non-oxide electrocatalysts such as oxalate, nitride, phosphide, selenide, sulfide, boride, etc. Liu et al. developed cobalt oxalate with a controllable microrod and micropolyhedron-like architecture for the alkaline OER purpose.<sup>7</sup> Wu and co-workers designed nanowire-like metallic Co4N for the same.8 Direct growth of Co<sub>2</sub>P supported on Co foil was demonstrated as a bifunctional catalyst for overall water splitting.9 Morphologically tuned Co<sub>0.85</sub>Se particularly for alkaline OER was reported by Li and co-workers.<sup>10</sup> In another study, a  $CoS_X$  hollow nanosphere was developed by an autoclaving method and showed 100% Faradaic efficiency for overall water splitting.<sup>11</sup> Amorphous Co<sub>2</sub>B was also employed for the alike purpose.<sup>12</sup> All these reports clearly claim that development of nonprecious nonoxide electrocatalysts is advantageous due to their prompt in situ transformation to generate the active species for the electrochemical water oxidation process.

Spinel-type  $Co_3O_4$  is well-known for their conductivity, long-term stability, and easy handling features.<sup>13,14</sup> Electrochemical OER performance of  $Co_3O_4$  can be tuned by numerous ways like morphological variation,<sup>15</sup> quantum dot design,<sup>16</sup> controlling porosity,<sup>17</sup> metal dopant,<sup>18</sup> defect generation,<sup>19</sup> conductive substance incorporation,<sup>20</sup> coupling with other materials,<sup>21</sup> and more. Metal ion dopants can effectively modify the electronic state of  $Co_3O_4$ , which further validates improved activity with prompt OER kinetics via lowering the charge-transfer resistance.<sup>22</sup> Transition metal selenides (TMSs) are exclusive for their extended metallicity. In addition, the comparatively larger size and less ionization energy of selenium (Se) make the corresponding transition metal selenides unique from other chalcogenides.<sup>23-25</sup> It is reported that electrochemical superiority of a catalyst can be boosted by hybridizing with another electrocatalyst. The synergistic effect of the microstructural interface would play the deliberate role to modulate the redox features via tuning the electrochemical surface area as well as active site density for a composite network. Among all the cobalt selenide polymorphs, nonstoichiometric Co<sub>0.85</sub>Se was widely employed for electrochemical applications owing to its intrinsic conductive nature, impressive capacity values, and layered structural defects.<sup>26,27</sup> Jin et al. reported the direct growth of CoFe LDH/Co<sub>0.85</sub>Se with a controllable nanosheet architecture on porous carbon cloth particularly for alkaline OER.<sup>2</sup> Self-supported electrocatalyst design has been captivated tremendously due to mechanical integrity, seamless contact, rapid charge transfer rate, and prudent active site distribution over the substrate network.<sup>29</sup> Xiong and co-workers prepared a Co-foam supported Co@CoTe2 porous framework showing excellent catalytic performance with long-term stability.<sup>30</sup> Most of the self-supported electrocatalysts have been prepared over expensive nickel or cobalt foam. The aforementioned approach has inspired us to design a self-supported electrocatalyst without using costly foam. Furthermore, a porous Co<sub>3</sub>O<sub>4</sub> microrod supported Co<sub>0.85</sub>Se/Co<sub>9</sub>Se<sub>8</sub> electrocatalyst is rarely reported in the literature for alkaline OER application.

In the present communication, we have prepared a  $Co_3O_4$  microrod supported  $Co_{0.85}Se/Co_9Se_8$  electrocatalyst and elucidated the synergistic role of the  $Co_3O_4$  network for OER in alkaline medium. For comparison, unsupported  $Co_{0.85}Se/Co_9Se_8$  was directly prepared under the same conditions and tested for OER. The synthesis strategy has

been optimized in such a way that exclusively retains the 1-D microstructure of the Co<sub>3</sub>O<sub>4</sub> supported Co<sub>0.85</sub>Se/Co<sub>9</sub>Se<sub>8</sub> network in the presence of nanograins. Under similar reaction conditions, unsupported Co<sub>0.85</sub>Se/Co<sub>9</sub>Se<sub>8</sub> delivers a flake-like architecture with numerous interparticle porosity. For the alkaline OER process, the overpotential requirement is found to be 400 and 330 mV for  $Co_3O_4$  and  $Co_3O_4/Co_{0.85}Se/Co_9Se_{81}$ respectively, to reach the benchmark 10 mA/cm<sup>2</sup><sub>geo</sub>. However, unsupported Co<sub>0.85</sub>Se/Co<sub>9</sub>Se<sub>8</sub> consumes 360 mV to reach the same. In addition, Co<sub>3</sub>O<sub>4</sub>/Co<sub>0.85</sub>Se/Co<sub>9</sub>Se<sub>8</sub> possesses a low Tafel slope, impressive stability, and a Faradaic efficiency of about  $\sim$ 82%. The electrochemical mechanism has been investigated with variation of pH and found to be primarily a proton decoupled electron transfer (PDET) mechanism. The superior performance of the supported electrocatalyst can be attributed to high double layer capacitance  $(C_{dl})$ , low chargetransfer resistance, and exposure of additional active sites present at the interlayer position. Postcatalytic analysis reveals formation of agglomerated nanograins and a nanoflake-like morphology, and scarcely any selenium (Se) has been recovered from EDS and XPS study. Despite having higher geometric performance for Co<sub>3</sub>O<sub>4</sub>/Co<sub>0.85</sub>Se/Co<sub>9</sub>Se<sub>8</sub>, the intrinsic activity is quite inferior compared to unsupported Co<sub>0.85</sub>Se/Co<sub>9</sub>Se<sub>8</sub>, indicating the contribution of abundant active site density toward improved geometrical activity. This work clearly authenticates the influence of the Co<sub>3</sub>O<sub>4</sub> support to modulate the alkaline OER performance of the Co<sub>0.85</sub>Se/ Co<sub>9</sub>Se<sub>8</sub> network by improving the exposure of active sites.

# 2. RESULTS AND DISCUSSION

First, a Co<sub>3</sub>O<sub>4</sub> microrod was synthesized by a ligand assisted route using cobalt nitrate hexahydrate and oxalic acid at room temperature in a water-ethanol medium, followed by calcination at 350 °C. The as-prepared Co<sub>3</sub>O<sub>4</sub> was further selenized under autoclaving condition at 180 °C for 12 h and washed with ethanol, followed by drying at room temperature (see details in the Experimental Section, Supporting Information). As shown in Figure S1, the XRD diffraction peaks around  $2\theta \sim 18.97^{\circ}$ , 22.84°, 30.38°, 35.14°, and 47.24° can be designated as (202), (004), (400), (022), and (602) planes, respectively, for CoC2O4·nH2O (sample S1, crystal system: orthorhombic, JCPDS File # 25-0250). After calcination treatment, the diffraction peaks at  $2\theta \sim 18.9^{\circ}$ , 31.24°, 36.94°, 38.61°, 44.74°, 55.74°, 59.54°, and 65.4° can be matched with (111), (220), (311), (222), (400), (422), (511), and (440) planes, respectively, for  $Co_3O_4$  (sample S2, Figure 1a-i, crystal system: cubic, JCPDS File # 43-1003). Selenization treatment further endows the appearance of  $Co_{0.85}Se$  and  $Co_9Se_8$  along with  $Co_3O_4$  for the as-prepared sample (sample S4, Figure 1a-ii). XRD signals observed at  $2\theta$ ~ 33.19°, 44.81°, 50.65°, 59.98°, 61.86°, 69.9°, and 71.35° can be resembled with (101), (102), (110), (103), (112), (202), and (004) planes, respectively, for  $Co_{0.85}Se$  (crystal system: hexagonal, JCPDS File # 52-1008). In addition, diffraction peaks at  $2\theta \sim 28.36^\circ$ , 29.68°, 49.36°, and 58.66° can be labeled to (311), (222), (440), and (622) planes, respectively, for Co<sub>9</sub>Se<sub>8</sub> (crystal system: cubic, JCPDS File # 01-089-4180). To understand the autoclaving effect during transformation from Co<sub>3</sub>O<sub>4</sub> to the Co<sub>3</sub>O<sub>4</sub>/Co<sub>0.85</sub>Se/Co<sub>9</sub>Se<sub>8</sub> composite network, phase analysis was performed for the as-prepared sample before autoclaving treatment. The corresponding XRD pattern reveals the appearance of  $CoSeO_3 \cdot nH_2O$  (sample S3, crystal system: monoclinic, JCPDS File # 25-0125) along with Co<sub>3</sub>O<sub>4</sub>

for the as-prepared sample just before autoclaving treatment (Figure S2). The aforementioned phase analysis clearly claims that, initially,  $Co_3O_4$  was transformed into  $Co_3O_4/CoSeO_3$ .  $nH_2O$  in a solution-phase reaction, followed by conversion into  $Co_3O_4/Co_{0.85}Se/Co_0Se_8$  under autoclave condition. For the unsupported sample, the diffraction pattern resembles with Co<sub>0.85</sub>Se and Co<sub>9</sub>Se<sub>8</sub> (sample S5, Figure 1a-iii). No diffraction peaks characteristic of elemental selenium (Se),  $\alpha$ -Co(OH)<sub>2</sub>, or Co<sub>3</sub>O<sub>4</sub> have been perceived for the as-prepared unsupported sample. In alkaline medium, elemental Se undergoes disproportionation reaction to produce  $Se^{2-}$  and  $SeO_3^{-2}$ , followed by the interaction with  $Co^{2+}$  to form  $Co_{0.85}$ Se and Co<sub>9</sub>Se<sub>8</sub> under autoclaving condition at 180 °C (Scheme S1).<sup>3</sup> <sup>33</sup> According to the Co-Se phase diagram, formation of  $Co^{2+}$  with octahedral coordination in  $Co_{0.85}$ Se is thermodynamically favorable compared to Co<sub>9</sub>Se<sub>8</sub> where cobalt is tetrahedrally coordinated in a lattice site.<sup>34</sup> However, reconstruction of the sublattice crystal structure from Co<sub>0.85</sub>Se to Co<sub>9</sub>Se<sub>8</sub> is kinetically labile because transformation of the coordination site does not lead to an extensive energy barrier for Co<sup>2+</sup>. We believe that Co<sup>2+</sup> at the tetrahedral site in spinel Co<sub>3</sub>O<sub>4</sub> facilitates the reconstruction of the sublattice via reducing the energy gap during selenization that further appears as prominent Co<sub>9</sub>Se<sub>8</sub> along with Co<sub>0.85</sub>Se for the supported catalyst under autoclaving condition.<sup>35</sup> The structural characteristics were further studied by FTIR analysis (Figure S3). The as-prepared sample shows a broad peak region at 1638 cm<sup>-1</sup> along with a peak-pair around 1312 cm<sup>-1</sup> (symmetric) and 1378 cm<sup>-1</sup> (asymmetric) representing the carbonyl vibrational mode for the oxalate group.<sup>5</sup> In addition, peaks appearing around 827 and 498 cm<sup>-1</sup> manifest the O-C-O asymmetric vibration mode and metal-oxygen vibration mode, respectively. The broad peak around 3378 cm<sup>-1</sup> visibly indicates the presence of structural water of  $CoC_2O_4 \cdot nH_2O$ (Figure S3-i). However, the annealed sample displays vibrational bands around 566 and 667 cm<sup>-1</sup>, indicating the Co-O stretching vibrational mode particularly for Co<sup>3+</sup> (coordinated at octahedral site of the spinel) and Co2+ (coordinated at tetrahedral site of the spinel), respectively (Figure S3-ii).<sup>36</sup> This clearly supports the formation of Co<sub>3</sub>O<sub>4</sub>, which is previously evidenced from XRD study. For the selenized sample, the vibrational spectrum shows weak peaks around 728  $cm^{-1}$ , indicating the Co-Se vibration mode along with a distinct Co<sub>3</sub>O<sub>4</sub> vibrational band. Furthermore, weaker peaks positioned around 1010 and 1347 cm<sup>-1</sup> represent O-H bending (in-plane) and stretching modes, respectively, for absorbed water molecules of the cobalt selenite complex (Figure S3-iii).<sup>37,38</sup> After autoclave reaction, the intensity of the vibrational band representing Co-Se around 714 cm<sup>-1</sup> is significantly increased. The sample also retains the vibrational bands at 1010 and 1347 cm<sup>-1</sup>. However, the observed Co-O vibrational peaks at 496 and 1608 cm<sup>-1</sup> clearly suggest the presence of a  $Co_3O_4$  structural unit within the  $Co_3O_4/$ Co<sub>0.85</sub>Se/Co<sub>9</sub>Se<sub>8</sub> composite network (Figure S3-iv). For the unsupported sample, the spectrum retains an intense vibrational band at 714 cm<sup>-1</sup> displaying strong Co-Se interaction. However, for template-free synthesis (i.e., unsupported sample), hardly any Co-O interaction is noted, revealing the absence of a  $Co_3O_4$  structural unit within the  $Co_{0.85}Se/Co_9Se_8$ composite network (Figure S3-v). The elemental state in the Co<sub>3</sub>O<sub>4</sub>/Co<sub>0.85</sub>Se/Co<sub>9</sub>Se<sub>8</sub> composite network was further studied by using XPS. The C 1s XPS spectrum shows peak positions at 284.2 and 291.1 eV, indicating C-C and C-F



Figure 2. FESEM images of as-prepared samples of (a)  $CoC_2O_4 \cdot 2H_2O$  (sample S1), (b)  $Co_3O_4$  (sample S2), (c)  $Co_3O_4/Co_{0.85}Se/Co_9Se_8$  (sample S4), and (d)  $Co_{0.85}Se/Co_9Se_8$  (sample S5).

interactions, respectively.<sup>5</sup> The observed peak for C-F is due to usage of a Nafion polymer as binder for the carbon paper supported dropcasted electrode (Figure 1b). As displayed in the Co 2p narrow scan, the appearance of two distinct peaks at 781.5 eV (Co  $2p_{3/2})$  and 797.5 eV (Co  $2p_{1/2})$  with the separation in binding energy (Co  $2p_{1/2} - Co 2p_{3/2}$ ) around 16.0 eV validates the existence of Co<sup>2+</sup> within the composite network.  $^{39}$  The binding energy values at 779.5 eV (Co  $2p_{3/2})$ and 795.8 eV (Co  $2p_{1/2}$ ) are ascribed to the presence of Co<sup>3+</sup>. In addition, the satellite peak at 785.8 eV clearly authenticates the coexistence of both Co2+ and Co3+, which is previously reported by Frost and co-workers (Figure 1c).<sup>40</sup> The binding energy values around 54.1 and 59.7 eV appear due to Se 3d and SeO<sub>xt</sub> respectively. Furthermore, deconvolution of the Se 3d peak manifests the binding energy values at 53.6 and 54.2 eV representing Se  $3d_{5/2}$  and Se  $3d_{3/2}$ , respectively (Figure 1d).<sup>41,42</sup> For the O 1s spectrum, peaks at 530.9, 532.08, and 534.6 eV can be attributed to lattice oxygen, a surface adsorbed hydroxyl group, and structural water molecules, respectively (Figure 1e).<sup>43</sup>

Microstructural characterization of samples was performed by FESEM study (Figure 2). For the as-prepared  $CoC_2O_4$ ·  $2H_2O$  sample, a uniform microrod-like architecture is obtained along with a smooth surface (Figure 2a). Nevertheless,  $Co_3O_4$ displays a porous network of 1-D microstructure with a rough

surface (Figure 2b). The microstructural change could be addressed due to nonequilibrium heat treatment at high temperature during annealing of the as-prepared CoC2O4. 2H<sub>2</sub>O sample. After selenization treatment, agglomerated nanograins along with a grainy rodlike framework is encountered for Co<sub>3</sub>O<sub>4</sub>/Co<sub>0.85</sub>Se/Co<sub>9</sub>Se<sub>8</sub> (Figure 2c). Close inspection further reveals a protrusion of nanograins over the surface of the 1-D microrod throughout the sample (Figure S4). For unsupported Co<sub>0.85</sub>Se/Co<sub>9</sub>Se<sub>8</sub>, the FESEM image displays a spongy flake-like morphology (Figure 2d). For further details of the microstructural appearance, TEM study was performed for all the samples. The CoC<sub>2</sub>O<sub>4</sub>·2H<sub>2</sub>O sample shows a microrod-like architecture with a diameter of about 60-200 nm and interplanar spacing of 0.25 nm representing the (022) plane from HRTEM study (Figure S5). Elemental mapping study with EDS shows a uniform distribution of C, Co, and O throughout the microrod architecture of  $CoC_2O_4$ .  $2H_2O$  (Figure S6). For Co<sub>3</sub>O<sub>4</sub>, the microrod-like architecture is retained along with interparticle porosity and long-range connectivity. However, pores are not uniform all over the oxide framework of the sample. The high-resolution image also discloses a stone-wall-like assembly which is formed from random particle aggregation maintaining a 1-D orientation (Figure S7). Elemental mapping and EDS study further show the distribution of Co and O all over the porous network



Figure 3. (a–d) TEM images, (e–h) elemental mapping, and (i) HRTEM image of grainy rodlike morphology of as-prepared  $Co_3O_4/Co_{0.85}$ Se/ $Co_9$ Se<sub>8</sub> (sample S4). (j) TEM image of agglomerated grainy network-like morphology, (k) HRTEM image from agglomerated nanograins, and (l, m) EDS study of  $Co_3O_4/Co_{0.85}$ Se/ $Co_9$ Se<sub>8</sub> (sample S4).

(Figure S8). For the  $Co_3O_4$  supported selenized sample, the coexistence of both nanograins and a grainy rod architecture is clearly perceived in the TEM investigation (Figure 3a). Close inspection reveals that the formation of nanograins took place from the edge of the porous rodlike architecture (Figure 3b,c). These nanograins are irregular in size and shape and aggregated in a random manner all over the network (Figure 3d). Additionally, uniform distribution of Co, Se, and O appeared from the elemental mapping study (Figure 3e-h). The HRTEM image shows lattice fringe with 0.20 and 0.24 nm representing the (102) and (311) planes for  $Co_{0.85}Se$  and  $Co_3O_4$ , respectively, at the interface of the grainy network (Figure 3i). For further confirmation, HRTEM study was also performed from the agglomerated network of the nanograinlike morphology (Figure 3j). From HRTEM analysis, interplanar distance appears around 0.20 nm, indicating the presence of  $Co_{0.85}$ Se for agglomerated nanograins (Figure 3k). EDS study further confirms the existence of Co, Se, and O throughout the composite sample (Figure 3l,m). However, morphological analysis is also investigated for the as-prepared sample before autoclaving treatment (Figure S9). The FESEM image represents a porous rodlike morphology along with aggregated particles throughout the framework (Figure S9a). TEM study displays a porous architecture with a stone-walllike assembly with interplanar spacing around 0.30 nm manifesting the (012) plane of CoSeO3.nH2O (Figure S9be). This clearly validates the transformation trajectory from Co<sub>3</sub>O<sub>4</sub> microrod to a Co<sub>3</sub>O<sub>4</sub>/CoSeO<sub>3</sub>·nH<sub>2</sub>O porous architecture during the selenization process, which is further transformed into the Co<sub>3</sub>O<sub>4</sub>/Co<sub>0.85</sub>Se/Co<sub>9</sub>Se<sub>8</sub> grainy network under autoclaving condition. Additional TEM study is also carried out to scrutinize the role of Co<sub>3</sub>O<sub>4</sub> as a self-supported framework. For the unsupported Co<sub>0.85</sub>Se/Co<sub>9</sub>Se<sub>8</sub> sample, the TEM image shows a spongy flake-like microstructure with numerous interparticle porosity (Figure 4a,b). Additionally, close inspection reveals that random alignment of flakes generates a crumpled thin-layer sheetlike architecture (Figure 4c). HRTEM study renders an interplanar separation of about 0.20 nm manifesting the (102) plane of the  $Co_{0.85}$ Se sample (Figure 4d). Elemental mapping using EDS analysis further indicates a uniform distribution of Co and Se all over the network (Figure 4e-h). Microstructural study fairly concludes the influence of a Co<sub>3</sub>O<sub>4</sub> microrod as a self-supported cobalt precursor toward the formation of a grainy network of the asprepared selenized sample.

Electrochemical activity for the alkaline oxygen evolution reaction (OER) was checked for all the carbon paper dropcasted samples using the *iR*-corrected backward LSV technique (Figure 5a). Among all the samples,  $Co_3O_4/Co_{0.85}Se/Co_9Se_8$  shows superior performance with a 330 mV overpotential for a benchmark current density of 10 mA/ cm<sup>2</sup><sub>geo</sub>, whereas 390, 400, and 440 mV are the required overpotential values for  $CoC_2O_4$ ·2H<sub>2</sub>O,  $Co_3O_4$ , and  $Co_3O_4/CoSeO_3·nH_2O$ , respectively.<sup>44</sup> To garner the role of  $Co_3O_4$ , unsupported  $Co_{0.85}Se/Co_9Se_8$  was also examined for electrochemical water oxidation reaction in alkaline medium.



Figure 4. (a-c) TEM images, (d) HRTEM image, (e-g) elemental mapping, and (h) EDS study of unsupported Co<sub>0.85</sub>Se/Co<sub>9</sub>Se<sub>8</sub> (sample S5).



Figure 5. (a) *iR*-corrected backward LSV scan of different electrocatalysts, (b) overpotential value to reach benchmark 10 mA/cm<sup>2</sup><sub>geo</sub> for different electrocatalysts, (c) Tafel slope analysis of different electrocatalysts, (d) Nyquist plots of different electrocatalysts, (e) backward LSV scan and (f) linear plot of current density of  $Co_{3}O_{4}/Co_{0.85}Se/Co_{9}Se_{8}$  (sample S4) with variation of pH.

Co<sub>0.85</sub>Se/Co<sub>9</sub>Se<sub>8</sub> exhibits a 360 mV overpotential value to reach the same 10 mA/cm<sup>2</sup><sub>geo</sub> (Figure 5b). To eliminate any uncertainty in the overpotential values, we have checked the accuracy and averaged the overpotential values along with the calculation of standard deviations and marginal errors for Co<sub>3</sub>O<sub>4</sub>/Co<sub>0.85</sub>Se/Co<sub>9</sub>Se<sub>8</sub> and Co<sub>0.85</sub>Se/Co<sub>9</sub>Se<sub>8</sub> samples (Figures S10 and S11, Table S1). These results clearly validate the importance of Co<sub>3</sub>O<sub>4</sub> microrods as a self-supported cobalt precursor to improve the water oxidation process. However, the unsupported catalyst also shows improved catalytic activity after calcination under an inert atmosphere with the distinct phase transition from  $Co_{0.85}Se/Co_9Se_8$  to  $CoSe_2$  (Figure S12). For further confirmation, CV measurements were performed with uncompensated solution resistance  $(R_u)$  correction in Figure S13. Just before checking the activity of  $Co_3O_4/$ Co<sub>0.85</sub>Se/Co<sub>9</sub>Se<sub>8</sub>, precondition of the working electrode was performed within 1.0-1.65 V at 50 mV/s until reproducible CV data were obtained in alkaline medium. In the first cycle of electrochemical precondition, a conspicuous redox wave is obtained, indicating the signature electrochemical features of the precatalyst while the intensity of the redox wave (oxidation peaks) is significantly abridged in the next cycle (Figure \$14).<sup>12</sup> Such transformation in the voltammogram manifests that the precatalyst is irreversibly transformed into species with higher oxidation states just after the first cycle. However, the conspicuous redox wave (reduction peaks) progressively appeared with enhanced intensity, suggesting continuous formation of oxidized cobalt species up to 20 cycles of precondition to achieve the steady state. During the cycling of cobalt selenide, two oxidation peaks were observed at 1.19 and 1.48 V, indicating  $Co^{2+}/Co^{3+}$  and  $Co^{3+}/Co^{4+}$  oxidation processes, respectively, for the corresponding catalytic network (Figure S15). The appearance of CoOOH can be assigned by the initial redox peak position, which is further turned into  $CoO_2$  representing formation of a  $Co^{4+}$  site during the electrochemical process (Scheme S2).<sup>45,46</sup> Interestingly, a catalytic center comprising Co4+ has been already mentioned as the primary active site for the alkaline OER mechanism. The distinct reduction peaks at 1.11 and 1.44 V are also encountered for the same. In addition, higher area under the CV curve suggests that the Co<sub>3</sub>O<sub>4</sub>/Co<sub>0.85</sub>Se/Co<sub>9</sub>Se<sub>8</sub> network possesses a higher number of active sites compared to Co<sub>0.85</sub>Se/Co<sub>9</sub>Se<sub>8</sub>. The as-displayed CV plot also represents that incorporation of  $Co_3O_4$  indeed facilitates the  $Co^{3+}/Co^{2+}$ transition and reducibility of the catalytic framework which further attributes higher active site density for the electrocatalyst in alkaline condition.47 The Tafel plot is further examined to interpret the kinetics of the alkaline OER process (Figure 5c). Co<sub>3</sub>O<sub>4</sub>/Co<sub>0.85</sub>Se/Co<sub>9</sub>Se<sub>8</sub> renders the Tafel slope value of about 91 mV/dec, which is lower in comparison with that of  $CoC_2O_4 \cdot 2H_2O$  (93 mV/dec),  $Co_3O_4$  (118 mV/dec), and Co<sub>3</sub>O<sub>4</sub>/CoSeO<sub>3</sub>·nH<sub>2</sub>O (134 mV/dec). Interestingly, the Tafel slope value for the composite network is even lower than that for unsupported Co<sub>0.85</sub>Se/Co<sub>9</sub>Se<sub>8</sub> (98 mV/dec), implying rapid charge transfer kinetics due to the presence of Co<sub>3</sub>O<sub>4</sub> within the composite network (Table S2).48 EIS (electrochemical impedance spectroscopy) measurements were further performed to measure charge-transfer resistance  $(R_{ct})$  of the electrocatalyst in alkaline medium (Figure 5d). The  $R_{ct}$  value is 2.687 ohm for Co<sub>3</sub>O<sub>4</sub>/Co<sub>0.85</sub>Se/Co<sub>9</sub>Se<sub>8</sub>, which is lower than that for  $CoC_2O_4$ ·2H<sub>2</sub>O (4.199 ohm),  $Co_3O_4$  (10.81 ohm),  $Co_3O_4/CoSeO_3 \cdot nH_2O$  (30.08 ohm), and  $Co_{0.85}Se/Co_9Se_8$ (3.698 ohm). The above study fairly endows the benefit of

 $Co_3O_4$  to accelerate charge transport features and conductivity of the selenized network. The experiment was also carried out in different pH mediums to investigate the mechanistic pathway of alkaline OER. The following mathematical relation can be used to calculate the proton reaction order ( $\rho$ RHE) for alkaline OER in the presence of the  $Co_3O_4/Co_{0.85}$ Se/Co<sub>9</sub>Se<sub>8</sub> composite network

$$\rho_{\rm RHE} = \left(\frac{\partial \log(j)}{\partial \rm pH}\right)_{\rm E} = -\left(\frac{\partial E}{\partial \rm pH}\right)_{j} / \left(\frac{\partial E}{\partial \log(j)}\right)_{\rm pH}$$

where  $\rho$ RHE is determined in RHE scale. Figure 5e shows consecutive increments in current density with increasing pH from 12 to 14. Furthermore, the  $\rho$ RHE value is estimated as 0.65 and 0.94 for Co<sub>3</sub>O<sub>4</sub>/Co<sub>0.85</sub>Se/Co<sub>9</sub>Se<sub>8</sub> and Co<sub>0.85</sub>Se/Co<sub>9</sub>Se<sub>8</sub>, respectively, indicating a proton decoupled electron transfer (PDET) assisted electrochemical water oxidation mechanism (Figures 5f and S16).<sup>27</sup> The mathematical expression of current for alkaline OER can be presented as

$$j = [OH^{-}].\theta.e^{-\Delta G/RT}$$

 $\theta$  refers to surface coverage which is predominantly comprised with \*OH or \*OOH sites, and [OH-] stands for the concentration of electrolyte. Thus, several factors like surface coverage ( $\theta$ ), pH of solution (concentration of [OH<sup>-</sup>]), and exponential parameter of adsorbed species are responsible for the sharp upsurge in current density with increasing pH of electrolyte medium. The  $\rho$ RHE value elucidates the mechanistic trajectory as OOH (ads) +  $OH^- \rightarrow OO$  (ads) +  $H^+$  +  $e^-$ , thereby indicating the prudent role of electrolyte concentration to drive the reaction via a decoupling mechanism.<sup>49,50</sup> To investigate the role of oxidized cobalt species, a five-step mechanistic pathway was proposed by Qiao and co-workers.<sup>3</sup> As shown in Scheme S3, a third step was recommended as the rate-determining step (RDS) which involves an oxyhydroxide (-OOH) intermediate. It was hypothesized that higher charge on Co species in the precatalyst electrostatically helps [OH<sup>-</sup>] adsorption, enabling the formation of the (-OOH)intermediate, followed by deprotonation to yield O2. In addition, electrochemical transformation from Co<sup>3+</sup> to Co<sup>4+</sup> is also involved during electrocatalysis that expedites the deprotonation of the oxyhydroxide (-OOH) intermediate to produce  $O_2$  in alkaline medium.<sup>52</sup> We also believe that  $Co^{3+}$ centers in Co<sub>3</sub>O<sub>4</sub> facilitate the formation of the oxyhydroxide (-OOH) intermediate, thereby reducing the energy gap for  $Co^{2+}/Co^{3+}$  and  $Co^{3+}/Co^{4+}$  transition favoring  $Co_3O_4/$ Co<sub>0.85</sub>Se/Co<sub>9</sub>Se<sub>8</sub> as a better electrocatalyst compared to Co<sub>0.85</sub>Se/Co<sub>9</sub>Se<sub>8</sub>. Interestingly, the geometrical current density value is found to be approximately 2 times higher for  $Co_3O_4/$ Co<sub>0.85</sub>Se/Co<sub>9</sub>Se<sub>8</sub> compared to Co<sub>0.85</sub>Se/Co<sub>9</sub>Se<sub>8</sub> in 1 (M) KOH, revealing the importance of the Co<sub>3</sub>O<sub>4</sub> support which exposes a higher number of active centers and interlayer active sites that further contribute in surface coverage ( $\theta$ ) for alkaline OER. The results also authenticate the benefit of Co<sup>3+</sup> as  $Co_3O_4$  in the precatalyst for the alkaline OER mechanism.

Electrochemical surface area (ECSA) measurement was studied to further illustrate the role of  $Co_3O_4$  within the selenized network. Recently, Surendranath et al. have reported a precise analytical method for double layer capacitance ( $C_{dl}$ ) calculation which is further employed to estimate the ECSA of a catalyst.<sup>53</sup> For  $Co_3O_4/Co_{0.85}$ Se/ $Co_9$ Se<sub>8</sub>, the  $C_{dl}$  value is about 8.19 mF/cm<sup>2</sup>, which is relatively higher than that for  $Co_{0.85}$ Se/ $Co_9$ Se<sub>8</sub> (1.08 mF/cm<sup>2</sup>), thereby indicating higher active site

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**Figure 6.** CV curves recorded at different scan rates to estimate double layer capacitance  $(C_{dl})$  for as-prepared samples of (a)  $Co_{3}O_{4}/Co_{0.85}Se/Co_{9}Se_{8}$  (sample S4) and (b)  $Co_{0.85}Se/Co_{9}Se_{8}$  (sample S5). (c) Linear fit for estimation of double layer capacitance  $(C_{dl})$  from DLC current vs scan rate plot. CV curves recorded at different scan rates to estimate active site density for as-prepared samples of (d)  $Co_{3}O_{4}/Co_{0.85}Se/Co_{9}Se_{8}$  (sample S4) and (e)  $Co_{0.85}Se/Co_{9}Se_{8}$  (sample S5). (f) Linear fit for estimation of active sites from  $Co^{2+}/Co^{3+}$  peak current vs scan rate<sup>1/2</sup> plot.

density in the presence of the self-supported Co<sub>3</sub>O<sub>4</sub> framework (Figure 6a-c).<sup>54</sup> For comparison, the  $C_{dl}$  value was also calculated for CoC2O4·2H2O, Co3O4, and Co3O4/CoSeO3·  $nH_2O$  samples (Figure S17). In addition, polarization curves of the electrocatalysts were normalized by their corresponding ECSA to understand the per site catalytic activity.<sup>55</sup> The obtained results clearly validate that unsupported Co<sub>0.85</sub>Se/ Co<sub>9</sub>Se<sub>8</sub> exhibits high per site catalytic activity compared to  $Co_3O_4/Co_{0.85}Se/Co_9Se_{87}$  whereas the per site activity is almost identical for both  $CoC_2O_4 \cdot 2H_2O$  and  $Co_3O_4$  (Figure S18). Despite having higher intrinsic efficiency for unsupported Co<sub>0.85</sub>Se/Co<sub>9</sub>Se<sub>8</sub>, geometrical OER performance is superior for Co<sub>3</sub>O<sub>4</sub> supported Co<sub>0.85</sub>Se/Co<sub>9</sub>Se<sub>8</sub> catalyst because of exposure of the higher number of active centers from the surface as well as bulk. For further clarity,  $C_{dl}$  measurement was also performed before precondition in alkaline medium. The as-prepared electrocatalyst shows a  $C_{dl}$  value of about 605.7 and 105.64 µF/cm<sup>2</sup> for Co<sub>3</sub>O<sub>4</sub>/Co<sub>0.85</sub>Se/Co<sub>9</sub>Se<sub>8</sub> and Co<sub>0.85</sub>Se/ Co<sub>9</sub>Se<sub>8</sub>, respectively, before electrochemical precondition (Figure S19). Such increments in  $C_{dl}$  value could be attributed to the formation of \*OH or \*OOH sites that further ensures change in surface coverage  $(\theta)$  during precondition of the precatalyst in alkaline medium. The change in C<sub>dl</sub> value is much higher in the presence of the  $Co_3O_4$  framework that may drive to form a higher number of accessible active sites in alkaline condition. It clearly authenticates the importance of the  $Co_3O_4$  precursor within the selenized network for improvement of geometrical OER activity. To elucidate further the electrochemical performance, intrinsic activity was compared for both the samples. Intrinsic activity of the sample is represented by TOF (turn over frequency) using the following mathematical equation:

$$\text{TOF} = j \frac{S_{\text{geo}}}{4Fm}$$

Here, F and S<sub>geo</sub> stand for Faraday constant (96 485 C/mol) and surface area (geometric area of substrate), respectively.<sup>56</sup> However, concentration of active species (m) can be estimated based on the position of accessible active sites in the catalytic matrix. To incorporate the geometric area value in TOF relation, substrate scope analysis was also conducted for the best catalyst over glassy carbon and porous carbon paper surfaces. Carbon paper dropcasted Co<sub>3</sub>O<sub>4</sub>/Co<sub>0.85</sub>Se/Co<sub>9</sub>Se<sub>8</sub> catalyst delivers greater mass activity compared to glassy carbon, conveying the advantage of carbon paper as a substrate due to its inherent porous network (Figure S20). The improved efficiency of the carbon paper dropcasted electrocatalyst may be originated due to spontaneous electrolyte penetration that exposes more active sites from the surface as well as the bulk of the catalytic framework. For the carbon paper dropcasted electrocatalyst, charge storage mechanism and position of active sites can be predicted by the following equations:

$$i = av^{b}$$
$$\log i = \log a + b \log v$$

"b" is estimated from the log *i* vs log *v* plot, where *i* and *v* stand for current and scan rate, respectively. Calculation of the "b" parameter endows the guidance about location of active sites within the catalytic framework. For  $b \sim 1$ , the surface controlled process predominates, while the diffusion process via ion intercalation is primarily responsible for  $b \sim 0.5$ .<sup>57</sup> CV measurements at different scan rates were performed for both Co<sub>3</sub>O<sub>4</sub>/Co<sub>0.85</sub>Se/Co<sub>9</sub>Se<sub>8</sub> and Co<sub>0.85</sub>Se/Co<sub>9</sub>Se<sub>8</sub> samples, and

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Figure 7. (a-c) FESEM and EDS images, (d-f) TEM images, (g) HRTEM image, and (h-k) elemental mapping of postcatalytic  $Co_{3}O_{4}/Co_{0.85}Se/Co_{9}Se_{8}$  (sample S4).

the "b" value was obtained from Co<sup>2+</sup>/Co<sup>3+</sup> oxidation current (Figure 6d,e). The calculated "b" is found to be 0.67 and 0.71 for Co<sub>3</sub>O<sub>4</sub>/Co<sub>0.85</sub>Se/Co<sub>9</sub>Se<sub>8</sub> and Co<sub>0.85</sub>Se/Co<sub>9</sub>Se<sub>8</sub>, respectively, manifesting the existence of additional active centers at interlayer positions in the presence of Co<sub>3</sub>O<sub>4</sub> (Figure S21). The CV plot further demonstrates a quasi-reversible process where separation potential ( $\Delta E_p$ ) is found to increase with increasing the scan rate value. Thus, active site concentration (*m*) can be calculated for the quasi-reversible process using the *i* vs  $\nu^{1/2}$  plot:

$$i = \pm 0.436 n FA_{\text{real}} C \frac{\sqrt{n FDv}}{RT}$$

Considering the same diffusion constant (*D*) value for both  $Co_3O_4/Co_{0.85}Se/Co_9Se_8$  and  $Co_{0.85}Se/Co_9Se_8$  samples, active site concentration ( $A_{real}C$ ) is estimated using D = 1 and n = 1, where  $A_{real}$  and *C* stand for electrochemical area and per site concentration, respectively.<sup>5,58</sup> The calculated concentrations of active species are  $3.078 \times 10^{-6}$  and  $1.796 \times 10^{-6}$  mol for  $Co_3O_4/Co_{0.85}Se/Co_9Se_8$  and  $Co_{0.85}Se/Co_9Se_8$ , respectively (Figure 6f). Nevertheless, the obtained TOF values are

0.0076 and 0.0102 s<sup>-1</sup> for Co<sub>3</sub>O<sub>4</sub>/Co<sub>0.85</sub>Se/Co<sub>9</sub>Se<sub>8</sub> and Co<sub>0.85</sub>Se/Co<sub>9</sub>Se<sub>8</sub>, respectively, at  $\eta$  = 400 mV. Despite having a higher intrinsic activity (TOF) for Co<sub>0.85</sub>Se/Co<sub>9</sub>Se<sub>8</sub>, geometrical activity is much superior for Co<sub>3</sub>O<sub>4</sub>/Co<sub>0.85</sub>Se/Co<sub>9</sub>Se<sub>8</sub>.<sup>59</sup> It indeed validates that higher geometrical activity of Co<sub>3</sub>O<sub>4</sub>/Co<sub>0.85</sub>Se/Co<sub>9</sub>Se<sub>8</sub> could be obtained due to presence of Co<sub>3</sub>O<sub>4</sub> which exposes a higher number of active centers and interlayer active sites that further contributes in surface coverage ( $\theta$ ) for alkaline OER.<sup>60</sup> The above results also reveal the importance of the self-supported Co<sub>3</sub>O<sub>4</sub> network for the selenization process to acquire a splendid OER electrocatalyst in alkaline medium.

The  $Co_3O_4/Co_{0.85}Se/Co_9Se_8$  composite network is further subjected for phase and microstructural analysis after electrochemical precondition. In Figure S22a, the XRD diffraction patterns of the  $Co_3O_4/Co_{0.85}Se/Co_9Se_8$  network before and after electrochemical precondition are shown. For further clarity, structural and phase analyses were also performed at successive preconditioning cycles (Figure S22b). Before electrochemical precondition, the carbon paper supported asprepared precatalyst shows signature diffraction peaks for



Figure 8. (a) Stability study with inset showing CV scan before and after stability test, (b) *iR*-corrected backward LSV scan before and after stability test with inset showing overpotential value for 10 mA/cm<sup>2</sup><sub>geo</sub>, (c) Nyquist plots before and after stability test, and (d) analysis of Faradaic efficiency for  $Co_3O_4/Co_{0.85}Se/Co_9Se_8$  (sample S4).

carbon paper (2 $\theta$  ~ 18.09°, 26.55°, 54.45°), Co<sub>3</sub>O<sub>4</sub> (2 $\theta$  ~  $18.9^{\circ}$ ,  $36.94^{\circ}$ ,  $38.61^{\circ}$ ),  $Co_{0.85}Se$  ( $2\theta \sim 33.19^{\circ}$ ,  $44.81^{\circ}$ ,  $50.65^{\circ}$ ), and  $Co_9Se_8$  (2 $\theta \sim 29.68^\circ$ , 49.36°). After the first cycle of precondition, hardly any diffraction peaks from Co<sub>3</sub>O<sub>4</sub> and Co<sub>0.85</sub>Se are detected, while the peaks from Co<sub>9</sub>Se<sub>8</sub> are retained. However, no significant change in elemental phase is observed from the first cycle to the 20th cycle during electrochemical precondition. These observations evidently claim the fact that electrochemical transformation into CoOOH is most likely occurring from the first cycle of precondition during electrolysis. For further confirmation, Raman measurement was performed to scrutinize the electrochemical transformation of the precatalyst during alkaline OER (Figure S23). The appearance of peaks positioned at 187.9, 454.2, 540.2, and 668.5 cm<sup>-1</sup> can be resembled with  $A_{g}$ ,  $E_{g}$ ,  $F_{2g}$ , and  $A_{1g}$ , respectively, indicating the presence of  $Co_{0.85}$ Se and  $Co_9Se_8$  for the as-prepared sample.<sup>61</sup> The signature peaks in the low frequency region at 187.9 and 258.5 cm<sup>-1</sup> stand for bending and stretching modes of Se-Se, respectively.<sup>62</sup> After the first cycle of electrochemical precondition, a conspicuous sharp peak appears at 462.7, 507.6, and 670.5 cm<sup>-1</sup>, divulging formation of CoOOH from the electrocatalyst.<sup>7</sup> It is worthy to state that no significant change is encountered from the 1st to the 20th cycle during electrochemical precondition that indeed suggests evolution of an active phase in initial segments of the catalysis in alkaline medium. To garner the elemental state of the postcatalytic sample, XPS measurement was also examined (Figure S24). Binding energy peaks from the C 1s plot around 284.6, 286.2, and 287.8 eV stand for the carbon paper. From the narrow scan of the Co 2p spectrum, the appearance of peaks at 780.4 (Co  $2p_{3/2})$  and 795.3 eV (Co  $2p_{1/2})$  implies the existence of a Co<sup>3+</sup> state with (Co  $2p_{1/2}$  – Co  $2p_{3/2}$ ) separation of about 15.1 eV. In addition, satellite peaks at 783.04 and 798.5 eV corroborate the same. Interestingly, hardly any distinct binding energy value is obtained from the Se 3d spectrum, revealing the absence of selenium species in the postcatalytic sample. Hu et al. have proposed in situ transformation of selenide to  $SeO_3^{-2}/SeO_4^{-2}$  that undergoes dissolution in 1 (M) KOH solution during electrocatalysis.<sup>63</sup> We believe that the selenide species etches out as K<sub>2</sub>SeO<sub>3</sub>/ K<sub>2</sub>SeO<sub>4</sub> with the formation of CoOOH during alkaline OER at pH = 14.<sup>64,65</sup> The etching of selenide was further evidenced by

## 3. CONCLUSION

Co<sub>3</sub>O<sub>4</sub> supported Co<sub>0.85</sub>Se/Co<sub>9</sub>Se<sub>8</sub> was synthesized by a twostep solution-based technique. In the first step, a Co<sub>3</sub>O<sub>4</sub> microrod was prepared by an oxalic acid assisted wet chemical process, followed by calcination at 350 °C. Thereafter, Co<sub>3</sub>O<sub>4</sub> microrods were selenized by an autoclaving method at 180 °C for 12 h. Phase investigation shows the formation of  $Co_{0.85}Se/$ Co<sub>9</sub>Se<sub>8</sub> in the presence of Co<sub>3</sub>O<sub>4</sub>, which is further supported by XPS analysis. Morphological study reveals the coexistence of nanograins and a grainy rodlike architecture throughout the network. It also discloses the protrusion of nanograins from the surface of Co<sub>3</sub>O<sub>4</sub> which is further supported by HRTEM analysis. Interestingly, Co3O4/Co085Se/Co3Se8 reaches the benchmark current density of 10 mA/cm<sup>2</sup><sub>geo</sub> with the need of an overpotential around 330 mV, whereas unsupported Co<sub>0.85</sub>Se/Co<sub>9</sub>Se<sub>8</sub> consumes 360 mV for the same, indicating the advantage of Co<sub>3</sub>O<sub>4</sub> microrods as the self-supported cobalt precursor. The improvement in catalytic property can be attributed on the basis of a change in ECSA  $(C_{dl})$  value, interlayer active sites (b value), and active center density for the alkaline OER. Despite having the higher geometrical activity, intrinsic performance is inferior for the  $Co_3O_4/$  $Co_{0.85}Se/Co_9Se_8$  network compared to unsupported  $Co_{0.85}Se/$ Co<sub>9</sub>Se<sub>8</sub>. Electrochemical study clearly demonstrates that the higher number of active centers could be the reason for extraordinary geometrical OER performance which is achieved in the presence of self-supported Co<sub>3</sub>O<sub>4</sub> microrods that further illustrates long-term stability, mechanical strength in different potential windows, and rapid charge transport properties. This study indeed addresses the utility of a metal oxide precursor with a controllable morphology in comparison with a common metal source to design the electrocatalytic framework for alkaline OER application. We also believe that the precursor modification approach can be employed for other selfsupported transition metal complexes regarding energy and environmental applications.

# ASSOCIATED CONTENT

#### **1** Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.0c02618.

XRD and FTIR patterns, FESEM and TEM images, elemental mapping and EDS, cyclic voltammograms (CV), corrected LSV patterns using the *iR*-compensation technique, double layer capacitance ( $C_{dl}$ ) measurement, comparative study with glassy carbon electrode, calculation of *b* value from scan rate and peak current plot, XRD and XPS analysis of postcatalytic sample, and multistep chronopotentiometric technique analysis (PDF)

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microstructural analysis and EDS study. FESEM images show the coexistence of particle and petal-like morphology throughout the postcatalytic network (Figure 7a,b). However, significant reduction in Se counts is conceived from EDS study that further supports previous XPS analysis for  $Co_3O_4/$ Co<sub>0.85</sub>Se/Co<sub>9</sub>Se<sub>8</sub> after electrochemical precondition (Figure 7c). The appearance of  $K^+$  in EDS further authenticates the elemental etching process during the alkaline OER mechanism. TEM investigation indeed renders agglomerated particles as well as a petal-like architecture along with long-range pore connectivity (Figure 7d-f). HRTEM analysis depicts an interplanar spacing of about 0.220 nm paving the presence of the (006) plane of CoOOH (Figure 7g, crystal system: rhombohedral, JCPDS File # 014-0673).<sup>5</sup> Elemental mapping further endows a uniform distribution of K, Co, and O all over the postcatalytic framework (Figure 7h-k). Furthermore, morphological evolution of the precatalyst was also studied at consecutive preconditioning cycles, indicating microstructural reformation is most likely occurring from the 1st cycle of precondition during electrolysis (Figure S25). Morphological study using FESEM and TEM clearly discloses the abrupt change in architecture after OER in alkaline medium. The change in the morphology into a petal-like network exposes the bulk of the material to the electrolyte, and thereby the Se species present in the bulk etches away along with the surface species. For bulk-scale application of the electrocatalyst, the  $Co_3O_4/$ 

Co<sub>0.85</sub>Se/Co<sub>9</sub>Se<sub>8</sub> network was further tested using a multistep chronopotentiometric method. It shows moderate stability at different potential ranges including 1.55 V for 15 min, thereby indicating excellent conductivity, charge transfer kinetics, and mechanical strength of electrode materials (Figure S26). The carbon paper dropcasted best catalyst was further examined by potentiodynamic cycling to ensure the stability issue.<sup>66</sup> To attain the benchmark 10 mA/cm<sup>2</sup><sub>geo</sub>, overpotential values are found to be 335, 340, and 360 mV after 10, 50, and 100 cycles, respectively, indicating only a slight decay in electrochemical performance after 100 cycles (Figure S27). It clearly represents that electrochemical features of Co<sub>3</sub>O<sub>4</sub>/Co<sub>0.85</sub>Se/Co<sub>9</sub>Se<sub>8</sub> are almost retained even after 100 cycles. A chronoamperometry technique was also performed to check 24 h stability test. Figure 8a shows near-identical activity even after 24 h usage which is further supported by CV analysis of the catalyst after the chronoamperometry experiment. The backward LSV scan (*iR*-corrected) manifests that the performance of the catalyst is slightly declined after the stability test. Thus, the postcatalytic Co<sub>3</sub>O<sub>4</sub>/Co<sub>0.85</sub>Se/Co<sub>9</sub>Se<sub>8</sub> network achieves 10 mA/cm<sup>2</sup><sub>geo</sub> at 1.575 V vs RHE that requires 15 mV more overpotential after long-term usage (Figure 8b). After stability test, charge-transfer resistance  $(R_{ct})$  is found to be 2.794 ohm, which is only slightly higher than that for the as-prepared catalyst (2.687 ohm). It indeed conveys near-identical charge transfer kinetics and catalytic activity without any loss of mechanical stability (Figure 8c). To scrutinize the ultimate electrochemical performance, Faradaic efficiency was also measured for the best sample, rendering ~82% efficiency for OER application in alkaline medium (Figure 8d). Catalytic performance of our best sample is also compared with the standard RuO<sub>2</sub> and earlier reported cobalt-based electrocatalyst representing akin activity in terms of *iR*-corrected backward LSV scan (Table S2).<sup>67-85</sup> This result also fortifies the bulk scale implementation of the Co<sub>3</sub>O<sub>4</sub>/Co<sub>0.85</sub>Se/Co<sub>9</sub>Se<sub>8</sub> framework as a commercial electrocatalyst for alkaline water oxidation purpose.

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#### Notes

The authors declare no competing financial interest.

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