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Evaluating DNA Derived and Hydrothermally Aided Cobalt Selenide **Catalysts for Electrocatalytic Water Oxidation**

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Supporting Information

ABSTRACT: Electrocatalysts with engaging oxygen evolution reaction (OER) activity with lesser overpotentials are highly desired to have increased cell efficiency. In this work, cobalt selenide catalysts were prepared utilizing both wetchemical route (CoSe and CoSe-DNA) and hydrothermal route (Co_{0.85}Se-hyd). In wet-chemical route, cobalt selenide is prepared with DNA (CoSe-DNA) and without DNA (CoSe). The morphological results in the wet-chemical route had given a clear picture that, with the assistance of DNA, cobalt selenide had formed as nanochains with particle size below 5 nm, while it agglomerated in the absence of DNA. The morphology was nano networks in the hydrothermally assisted



synthesis. These catalysts were analyzed for OER activity in 1 M KOH. The overpotentials required at a current density of 10 mA cm⁻² were 352, 382, and 383 mV for Co_{0.85}Se-hyd, CoSe, and CoSe-DNA catalysts, respectively. The Tafel slope value was lowest for Co_{0.85}Se-hyd (65 mV/dec) compared to CoSe-DNA (71 mV/dec) and CoSe (80 mV/dec). The chronoamperometry test was studied for 24 h at a potential of 394 mV for Co_{0.85}Se-hyd and was found to be stable with a smaller decrease in activity. From the OER study, it is clear that $Co_{0.85}$ Se was found to be superior to others. This kind of related study can be useful to design the catalyst with increased efficiency by varying the method of preparation.

INTRODUCTION

The usage of fossil fuels with the increased demands for harvesting energy has made catastrophic changes to the climate and affected the environment much. To overcome this issue, hydrogen is triggered to be a "future fuel" and currently produced to the maximum by steam reforming of fossil fuels.^{1,2} For the greener production of energy, renewable energy sources assisting hydrogen production is desired in large scale to exclude the carbon emitting fuels to the environment.³ With the electrolysis of water, hydrogen can be produced with ease but lacks in the commercial scale due to the complex OER at the anode.^{4,5} In electrolysis of water, the OER with four proton and electron coupled reactions drag more overpotential to drive the reaction.⁶ In HER, it involves electrochemical adsorption of hydrogen ions and is followed by chemical or electrochemical desorption of a hydrogen molecule from the electrode surface.⁷ Finding a catalyst with increased efficiency in OER is a bottleneck to the development of water electrolysis. So far, IrO2 and RuO2 have been investigated as better catalysts for OER, but fading of catalysts such as IrO3 and RuO4 to the electrolyte for long-term usage restricts its commercial application, in addition to the material cost.^{8,9}

Therefore, finding earth abundant based catalysts with better activity and superior stability for long-term application with continuous production remains a challenge till date.³

The transition metals based catalysts have recently attracted the researchers for their enhanced activity, notably, in alkaline medium.^{10–14} Transition metals as oxides have been studied a lot, and recently, chalcogenides have showed tremendous activity with respect to the changes in stoichiometry.^{15–17} Also, the effect of oxy-hydroxides and oxides of Co and Fe as CoOOH, FeOOH, and $CoFe_2O_4$ are studied for OER.^{18–21} In chalcogenides, among sulfides and selenides, selenides are highly active for both OER and HER, respectively.²²⁻²⁴ Careful literature survey suggests that the selenides were combined with Co, Ni, and Fe and studied as single and mixed metallic selenides for enriched activity and stability.^{25–42} Recently, cobalt-based selenides were studied with different stoichiometric ratios such as Co₇Se₈ and Co_{0.85}Se and also with other metals like Ni and Fe as CoO_x -CoSe, $Co_{1-x}Fe_xSe_2$, and Ni_{0.33}Co_{0.67}Se₂, respectively, for enriched water oxidation

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applications with better results.^{25–42} These kinds of transition metals based catalysts had delivered superior stability in alkaline medium.^{43,44} In addition to this, there are also reports highlighted the formation of Ni, Fe and Cu based selenides prepared in different experimental conditions for both electrocatalytic OER and HER applications in different media.^{37,42,45}

With different methods of synthesis of cobalt selenide catalysts, namely, hydrothermal, electrodeposition, and wet chemical synthesis, the wet-chemical route is easy to prepare within a short span of time. The utilization of bioscaffolds like DNA in the synthesis of cobalt selenide catalysts was not explored yet. DNA with the aromatic base pairs and A-T and G-C pairing give a perfect assembly to anchor the metal-based nanoparticles (NPs) over the surface of DNA.46,47 This kind of report has already been well explored. From the previous literature survey, it has been found that DNA with negative charges along with nucleobases provides a great platform for anchoring positive metal ions via a simple electrostatic interaction.48 From the DNA-templated synthesis, it is the interaction of positive metal ions with the polyanionic backbone of DNA is the initial step. Therefore, it is possible to design different inorganic materials by adding reducing agents or others to this assembly. Based on this, there are different reports highlighting the DNA-assisted formation of metal NPs by chemical reduction, photoreduction, and electrodeposition methods.⁴⁸ Different sources of DNA can be exploited for the formation of inorganic materials by finetuning the concentration of DNA.⁴⁸ Recently, sulfides of Co and Ni have also been prepared with the assistance of DNA and applied in OER studies. The use of DNA assists the anchoring of Co²⁺ over the DNA assembly and forms as sulfides of CoS and NiS over DNA.^{22,49} The use of DNA has been reported as a binder and as scaffold from earlier studies.²² In general, the presence of phosphate moieties are found to enhance the OER kinetics, as observed from the literature studies.^{50,51} In CoS-DNA work also, the presence of phosphates with high concentration of DNA ensured better activity at higher anodic overpotentials. At lower overpotentials, CoS-DNA with a lower concentration of DNA (0.036 M) showed better activity, and at higher overpotentials, the CoS-DNA with high concentration (0.084 M) outperformed it. This gives a clue that with a high concentration of DNA with phosphates, at higher overpotentials, the activity may be enhanced.²² Here, the presence of phosphate groups from DNA could also tend to synergistically enhance the electron transfer kinetics at the interface. Previously, metalbased NPs have successfully anchored over the DNA by our group.^{22,52} Hence, use of DNA in the synthesis of cobalt selenide based catalysts will be interesting and also will tend to improvise the activity at higher overpotentials in OER.

In this present work, the comparative OER study on the cobalt selenide catalysts prepared in both wet-chemical and hydrothermal conditions were analyzed. Moreover, the influence of DNA as a scaffold and synergetic enhancement in OER activity has also been observed at higher overpotentials compared to only CoSe prepared in the wet-chemical route, which was in accordance with the previous report on the DNA-based CoS catalysts.²² The morphology was varied with respect to the method adopted for the synthesis of cobalt selenides. With the assistance of DNA, cobalt selenide had formed as nanochains with a particle size below 5 nm and agglomerated when prepared without DNA. The morphology

was nano networks in the hydrothermally assisted formation of Co_{0.85}Se-hyd. These catalysts were analyzed for OER activity in 1 M KOH to prove their potentiality. The overpotentials required at a current density of 10 mA cm⁻² were 352, 382, and 383 mV for Co_{0.85}Se-hyd, CoSe, and CoSe-DNA catalysts, respectively. Presence of phosphate groups in DNA enhanced the activity of the CoSe catalyst, specifically at higher overpotentials during OER. The Tafel slope value was lowest for Co_{0.85}Se-hyd (65 mV/dec) compared to CoSe-DNA (71 mV/dec) and CoSe (80 mV/dec), respectively, that showed that the charge transfer kinetics was facile in Co_{0.85}Se-hyd. The potentiostatic analysis further confirmed that Co_{0.85}Se-hyd, CoSe-DNA, and CoSe were stable, with a minimal decrease in activity for 24 h. The combined study clearly reveals that Co_{0.85}Se-hyd showed better activity and stability compared to the others.

EXPERIMENTAL SECTION

Synthesis of CoSe-DNA, CoSe, and Co_{0.85}Se-hyd. To prepare CoSe-DNA, 0.13 g of selenium is added to the solution of H_2O that contains 0.048 M of DNA. Simultaneously, 0.25 g of NaBH₄ is added and stirred vigorously to form a clear solution of NaHSe in DNA. Once the colorless solution is formed, 0.54 g of CoAc₂ is added to the solution, and immediately, the solution turns dark black, inferring the nucleation of CoSe over DNA. The stirring continued for 30 min to ensure complete formation of CoSe, and the settled CoSe is washed with DI water several times to exclude sodium ions and was dried in the oven for 60 °C for 12 h.

From Scheme 1, we can see that, at first, when Co^{2+} ions are added to the DNA, there is a binding of Co^{2+} ions that occur by means of

Scheme 1. Schematic Representation of Anchoring of Co²⁺ Ions over DNA and Subsequent Formation of CoSe-DNA



electrostatic interactions with negative base pairs and nucleobases present in DNA. After forming an assembly of Co^{2+} -DNA by simple stirring, the subsequent addition of NaHSe resulted in the formation of CoSe-DNA nanochains. This kind of related study is well observed by us and others previously.^{22,46,47,49,52} Following a similar strategy, only CoSe is prepared, excluding the addition of DNA. For Co_{0.85}Sehyd, 0.54 g of CoAc₂ is added to the solution of ascorbic acid (1.4 g) in 30 mL of H₂O. The whole solution is added to 0.13 g of selenium and 0.25 g of NaBH₄ in 50 mL of H₂O and kept in an autoclave at 200 °C for 24 h. After this, the collected Co_{0.85}Se-hyd was washed with DI water several times and it is dried in the oven for 60 °C for 12 h. The reagents used during the synthesis, the sample preparation techniques for different characterizations, and details about the instrument specifications for electrochemical studies have been provided in the Supporting Information (SI).

Electrochemical Characterizations. The prepared CoSe-DNA, CoSe, and Co_{0.85}Se-hyd catalysts were subjected for electrocatalytic OER studies in 1 M KOH. The working electrodes for electrocatalytic studies prepared using 3 mg samples with H_2O , nafion, and ethanol were taken in a ratio (7.5:2:0.5) and sonicated to form a slurry solution and are coated on a carbon fiber cloth (CC) substrate that



Figure 1. (a) X-ray diffraction pattern of CoSe-DNA and (b) the XRD pattern of CoSe-hyd.

had dimensions of 4 × 0.5 cm and dried at 60 °C for 2 h. An Hg/ HgO reference electrode, Pt counter electrode, and cobalt selenide working electrodes were used in 1 M KOH, and the corresponding loading of the catalyst is 0.205 mg cm⁻². Polarization curves were acquired at a sweep rate of 5 mV s⁻¹ and 100% *iR* compensation were done manually from the $R_{\rm s}$, as observed from EIS. To ensure the stability of the as-prepared catalyst, continuous potentiostatic electrolysis was done at a potential of 394 mV for 24 h and also by accelerated degradation (AD) studies at a very high sweep rate of 200 mV s⁻¹ for 500 cycles in 1 M KOH. The electrochemical impedance spectroscopic (EIS) analysis was carried out in the frequency range of 1 Hz to 100 kHz with an amplitude potential of 0.05 V. The potential scale of all the observed electrochemical results were converted into reversible hydrogen electrode scale (RHE) following earlier literature reports.⁵³

RESULTS AND DISCUSSION

Characterization of CoSe-DNA and $Co_{0.85}$ Se-hyd Catalysts. Various advanced characterization tools were used to analyze the confirmation of the samples prepared.

Figure 1 showed the X-ray diffraction analysis for both CoSe-DNA and Co_{0.85}Se-hyd. Figure 1a shows no characteristic information since there is no identifiable peak observed. This gives information that the DNA-aided formation of CoSe can be either amorphous in nature or the particle size would be too small to diffract the incident X-ray beam. From Figure 1b, which is for Co_{0.85}Se-hyd, shows three humps at 33.3, 44.7, and 51.6° that exactly matched with Co_{0.85}Se with ICDD No. 00-052-1008.²⁹

Likewise, XRD pattern of only CoSe that was prepared in the wet-chemical route, showed a peak near 37.5° that matched with CoSe in accordance with the ICDD No. 00-015-0464 (shown in Figure S1 in the SI). After this, to have information on the morphology, transmission electron microscopy (TEM) was carried out and shown here as Figure 2 for CoSe-DNA and as Figure 3 for Co_{0.85}Se-hyd. From Figure 2a-c, the DNA with a chain-like structure can be seen with increasing magnification and CoSe NPs decorated over it with the size around 5 nm. Similar kinds of DNA-based metal NPs and metal sulfides were prepared earlier from our group.^{22,48} Figure 2d is the high resolution transmission electron microscopy image that showed clear assembly of CoSe NPs decorated over the surface of DNA chain. Figure 2e is the lattice fringes observed at higher magnifications and from the d-spacing, plane was observed to be (002) that was related to the JCPDS file No. 01-089-2004 as seen from the inset of the



Figure 2. (a-c) Low and high magnified TEM images of CoSe-DNA; (d) HRTEM image at high magnification; (e) HRTEM image with lattice fringes; and (f) SAED pattern.



Figure 3. (a-d) Low and high magnified TEM images of $Co_{0.85}$ Sehyd and (e) the corresponding SAED pattern.

figure. The selected area diffraction (SAED) from Figure 2f shows diffused ring pattern as the particle size is too small to diffract the electron beam. The plane corresponding to CoSe has been calculated from the radius of ring that was compared with the JCPDS file No. 01-089-2004. From the micro-structural study, it is clear that the formed CoSe has grown over the DNA chain and the size was below 5 nm.²² Similarly, for Co_{0.85}Se-hyd, TEM images were analyzed, and from Figure

3a-d, we can see low and high magnified images of $Co_{0.85}Se$. They show agglomerated particles with a size varying around 20 nm and has formed as nanonetworks with particles being agglomerated. The SAED pattern shows polycrystalline nature (Figure 3e).

For comparison, TEM images of only CoSe prepared in wetchemical route have been provided as Figure S2 in the SI. From the images of Figure S2a-d, it is clear that the formed CoSe NPs get agglomerated and formed as nanoburls. The SAED pattern observed was diffused ring pattern similar to that of CoSe-DNA (Figure S2e). From these micrographs, it is proved that with the absence of DNA, CoSe formed is agglomerated whereas in the presence of DNA, it is assembled over the surface of DNA to form nanochain assemblies of CoSe-DNA. The comparative microstructural analysis revealed that, with the method of preparation, the resulting morphology was also varied, and particularly, in the wet-chemical route, DNA has exclusively formed chain-like morphology and, without DNA, it is agglomerated.

To further ascertain the presence of DNA along with CoSe in CoSe-DNA, high angle annular dark field (HAADF) mapping was carried out in the HR-TEM mode and is given here as Figure 4. From Figure 4a, the image clearly shows the



Figure 4. (a) Area taken for HAADF mapping and (b-f) the mapping of Co, Se, N, P, and O (K shells), respectively.

CoSe-DNA nanochains where HAADF mapping was carried out. From Figure 4b-f, the presence of Co, Se, N, P, and O K shells further ascertain the CoSe-DNA assemblies.²² From these analyses it is clear that CoSe is assembled over DNA to form CoSe-DNA nanochains. After the morphological studies, the chemical nature of both CoSe-DNA and Co_{0.85}Se-hyd were analyzed by X-ray photoelectron spectroscopy (XPS). The XPS study of CoSe-DNA has been provided here as Figure 5. From Figure 5a, which is for a Co 2p high resolution spectrum, two characteristic peaks are shown that are due to the spinorbit coupling and observed as Co $2p_{3/2}$ and Co $2p_{1/2}$ respectively. It shows peaks at 781 and 796.2 eV that corresponded to the +2 oxidation state of Co from CoSe-DNA.⁴⁴ The peaks arrived at the higher binding energy values, which were the respective satellite peaks of the same. Similarly, for Se 3d high resolution spectrum (Figure 5b), Se $3d_{5/2}$ and Se $3d_{3/2}$ were observed at binding energy values of 54.4 and 57.6 eV, respectively. The O 1s spectrum (Figure 5c) shows two peaks at binding energy values of 530.1 and 533.2 eV that correspond to the moisture and some oxides of Se over the surface.⁴⁴ Figure 5d is for N 1s that is observed from the

presence of a heteroatom N from base pairs of DNA. Similarly, from Figure 5e, P 2p is present as P $2p_{3/2}$ and P $2p_{1/2}$, further confirming the components of DNA in CoSe. C 1s from Figure 5f showed peaks for C-O, C-OH, and C-C bonds from DNA at different binding energies. These results clearly confirm the presence of DNA along with CoSe and forms assembly of CoSe-DNA.²² Similarly, for Co_{0.85}Se-hyd also, XPS analysis was performed and is provided as Figure S3 in the SI. Figure S3a, which is for the Co 2p high resolution spectrum, shows peaks for 780.5 and 796.3 eV, which are for Co 2p_{3/2} and Co 2p_{1/2}, respectively, along with characteristic satellite peaks.²⁹ For the Se 3p high resolution spectrum (Figure S3a), peaks observed for 164.4 and 170.2 eV confirmed the presence of selenium with surface oxides. For the O 1s spectrum (Figure S3c), it showed peaks for H₂O, OH, and SeO₂ functionalities at binding energy values of 530.3, 531.1, and 534.5 eV, respectively. These results together confirm the formation of CoSe catalysts prepared at different conditions with concurrent observation.

Electrocatalytic Water Oxidation Studies of CoSe-DNA, CoSe, and Co_{0.85}Se-hyd Catalysts. The electrocatalytic water oxidation studies were carried out in a conventional three electrode system in 1 M KOH where cobalt selenide was used as a working electrode, Hg/HgO as reference, and Pt as counter electrodes.

The LSV curves were *iR* corrected 100% manually and have been shown here as Figure 6. The LSV curves from Figure 6a show that for attaining a current density of 10 mA cm^{-2} , Co_{0.85}Se-hyd had required an overpotential of 354 mV, while CoSe-DNA and only CoSe had required 382 and 383 mV, respectively. A closer look at the figure shows that, at higher overpotentials, the activity of CoSe-DNA was enhanced much due to the presence of phosphate groups from DNA that could synergistically enhance the OER performance, similar to the previous reports.²² The Tafel slopes (Figure 6b) extracted from the LSV curves were lowest for Co_{0.85}Se-hyd that shows 65 mV/dec, while CoSe-DNA and CoSe show 71 and 80 mV/ dec, respectively. From LSV and Tafel slopes, it has been observed that the OER activity was superior in the case of Co_{0.85}Se-hyd, however, at higher overpotentials, the activity of CoSe-DNA was enhanced, indicating the influence of DNA in the CoSe catalyst. The accelerated degradation (AD) study was carried out at a high scan rate of 200 mV/s for 500 cycles in all three catalysts, and the LSV curves acquired after AD test have been given here as Figure 6c. The increase in overpotentials at a same current density of 10 mA cm⁻² was 62, 50, and 39 for CoSe-DNA, CoSe, and Co_{0.85}Se-hyd. This shows the better stability of the prepared catalysts even at higher scan rates for more cycles. These kinds of seleniumbased catalysts were reported earlier and showed promising stability.43,44 Hence, from the AD test it is clear that the stability was comparatively high, even at such a rapid scan rate of 200 mV/s. Moreover, as an important tool to test the realtime stability of a catalyst, potentiostatic analysis was carried out for all three catalysts for 24 h and were found to be stable, with very less degradation in activity from a current density of 10 mA cm⁻² (Figure 6d). In addition to this, electrochemical impedance study was carried out at an overpotential of 424 mV and is provided as Figure S4. In general, at higher overpotentials, the electron transfer rate will be too fast and therefore the observed R_{ct} changes will be less. Here, the charge transfer resistance values as can be seen from the image were in between 8 and 12 Ω (Figure S4a) in all the cases that



Figure 5. (a) Co 2p high resolution spectra; (b) high resolution spectra of Se 3d; and (c) O 1s, (d) N 1s, (e) P 2p, and (f) C 1s high resolution spectra, respectively.

showed the increased activity of CoSe catalysts at a high anodic potential. After the AD test also, the R_{ct} values were in the range of $12-20 \Omega$ (Figure S4b) for CoSe-DNA, CoSe, and Co_{0.85}Se-hyd catalysts, respectively. From an EIS study, it is clear that Co_{0.85}Se was found to be superior to the other two catalysts. Moreover, electrochemical surface area (ECSA) was measured by double layer capacitance method (C_{dl}) . The plot between $\Delta j(j_a - j_c)$ versus scan rate is portrayed as Figure S5 in the SI. Among three catalysts, the C_{dl} value was higher for $Co_{0.85}$ Se-hyd, with a value of 0.92 μ F, while comparing the other two CoSe-DNA (0.5 μ F) and CoSe (0.3 μ F), respectively. From the electrochemical studies, it has been observed that the Co_{0.85}Se-hyd catalyst has shown better activity than the other two catalysts. However, CoSe-DNA at higher overpotentials could deliver better activity that stresses the role of DNA in enhancing the electrocatalytic activity while

comparing other catalysts. After the OER studies, the structural changes have been monitored by XRD and Raman spectral studies first and is given in the SI as Figures S6 and S7. From Figure S6a, the peak observed at 37.5° was attributed to the CoO phase formed during OER and well matches with the ICDD file No. 042-1300. The peak at 31.7° was due to the Se and O₂ formed after OER that matched with the ICDD file No. 01-083-2439. Figure S6b was again confirming the peaks of carbon cloth used as a substrate for the electrochemical studies. The formation of CoO phase during OER is again confirmed with Raman spectra and showed peaks for the Co_{0.85}Se and CoO after OER.^{54,55} The peaks observed at 117 and 674 cm⁻¹ were corresponded to the Co_{0.85}Se and CoO and is in accordance with the earlier reports (Figure S7). The morphological robustness of Co_{0.85}Se-hyd was monitored with HR-TEM analysis and shown as Figure S8a-d in the SI. As



Figure 6. (a) *iR* corrected LSV at a scan rate of 5 mV/s, (b) Tafel slope extracted from LSV, (c) LSV after accelerated degradation test, and (d) the chronoamperometry study for 24 h at 394 (Co_{0.85}Se-hyd) and 444 mV (CoSe-DNA and CoSe).

observed from Figure S8a-c, the morphology was still like agglomerates of Co_{0.85}Se with a sheet-like structure. This could be attributed to the electrode preparation method, oxide phase formed during OER, and also, the sample preparation method for HR-TEM analysis (sonication) that deliberately resulted in the agglomerated sheets of Co_{0.85}Se. Figure S8d showed the polycrystalline nature of the catalyst after OER. To further ensure the presence of elements after the OER studies, HAADF color mapping was carried out for Co_{0.85}Se and has been given as Figure S9a-d in the SI. Figure S9a and b are the images of area taken and the mixture of mapping of Co, Se, and O, respectively. Moreover, the presence of Co, Se, and O is well observed from the individual K shell mappings of Co, Se, and O from Figure S9c-e, respectively. These findings clearly stress that, even though selenium is leached as SeO₂ during anodization, even after 24 h of PSTAT analysis, still the presence of Co and Se is observed that showed the material robustness at harsh anodic conditions.^{43,44}

CONCLUSION

To summarize, cobalt selenide is prepared in three methods, namely, with and without DNA in wet-chemical route and without DNA in hydrothermal route. All three catalysts have shown different morphological features. The potentiality of three catalysts was analyzed for electrocatalytic OER in 1 M KOH. From OER study, at a current density of 10 mA cm⁻², the Co_{0.85}Se-hyd required a very low overpotential of 354 mV. The CoSe-DNA and CoSe required 382 and 383 mV, respectively, at the same current density. The Tafel slope, AD test, and potentiostatic analyses clearly gave information

that $Co_{0.85}$ Se-hyd was the most active one compared to the other two. Between CoSe-DNA and only CoSe, the activity was enhanced in the former one because of the influence of DNA. With our present synthesis methods, CoSe-DNA proved to be more advantageous compared to $Co_{0.85}$ Se-hyd and is found to be the most optimal catalyst, with a significant increase in efficiency. From OER studies, it is the $Co_{0.85}$ Se-hyd catalyst that was found to be better than other catalysts in terms of activity and stability. In the future, similar chalcogenide-based catalysts can be derived from DNA for increased OER activity.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.9b00354.

Information on the materials used and the sample preparation for various characterization techniques and figures related to electrochemical studies (PDF)

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Notes

The authors declare no competing financial interest.

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REFERENCES

(1) Garland, N. L.; Papageorgopoulos, D. C.; Stanford, J. M. Hydrogen and fuel cell technology: Progress, challenges, and future directions. *Energy Procedia* **2012**, *28*, 2–11.

(2) Edwards, P. P.; Kuznetsov, V. L.; David, W. I. F.; Brandon, N. P. ydrogen and fuel cells: towards a sustainable energy future. *Energy Policy* **2008**, *36* (12), 4356–4362.

(3) Wendt, H.; Imarisio, G. Nine years of research and development on advanced water electrolysis. A review of the research programme of the Commission of the European Communities. *J. Appl. Electrochem.* **1988**, *18*, 1–14.

(4) Dau, H.; Limberg, C.; Reier, T.; Risch, M.; Roggan, S.; Strasser, P. The mechanism of water oxidation: from electrolysis via homogeneous to biological catalysis. *ChemCatChem* **2010**, *2* (7), 724–761.

(5) Yan, Y.; Xia, B. Y.; Zhao, B.; Wang, X. A review on noble-metalfree bifunctional heterogeneous catalysts for overall electrochemical water splitting. *J. Mater. Chem. A* **2016**, *4* (45), 17587–17603.

(6) McCrory, C. C. L.; Jung, S.; Peters, J. C.; Jaramillo, T. F. Benchmarking heterogeneous electrocatalysts for the oxygen evolution reaction. J. Am. Chem. Soc. **2013**, 135, 16977–16987.

(7) You, B.; Jiang, N.; Sheng, M.; Sun, Y. Microwave vs solvothermal synthesis of hollow cobalt sulfide nanoprisms for electrocatalytic hydrogen evolution and supercapacitors. *Chem. Commun.* **2015**, *51*, 4252–4255.

(8) Yagi, M.; Tomita, E.; Sakita, S.; Kuwabara, T.; Nagai, K. Self-Assembly of Active IrO_2 Colloid Catalyst on an ITO Electrode for Efficient Electrochemical Water Oxidation. *J. Phys. Chem. B* **2005**, *109* (46), 21489.

(9) Anantharaj, S.; Kundu, S. Self-Assembly of Active IrO_2 Colloid Catalyst on an ITO Electrode for Efficient Electrochemical Water Oxidation. *Curr. Nanosci.* **201**7, *13* (4), 333–341.

(10) Ganesan, P.; Sivanantham, A.; Shanmugam, S. Inexpensive electrochemical synthesis of nickel iron sulphides on nickel foam: super active and ultra-durable electrocatalysts for alkaline electrolyte membrane water electrolysis. *J. Mater. Chem. A* **2016**, *4* (42), 16394–16402.

(11) Yeo, B. S.; Bell, A. T. Enhanced activity of gold-supported cobalt oxide for the electrochemical evolution of oxygen. *J. Am. Chem. Soc.* **2011**, *133* (14), 5587–5593.

(12) Tran, P. D.; Chiam, S. Y.; Boix, P. P.; Ren, Y.; Pramana, S. S.; Fize, J.; Artero, V.; Barber, J. Novel cobalt/nickel-tungsten-sulfide catalysts for electrocatalytic hydrogen generation from water. *Energy Environ. Sci.* **2013**, *6* (8), 2452.

(13) Zhang, Y.; Gao, T.; Jin, Z.; Chen, X.; Xiao, D. A robust water oxidation electrocatalyst from amorphous cobalt–iron bimetallic phytate nanostructures. *J. Mater. Chem. A* **2016**, *4* (41), 15888–15895.

(14) Yang, L.; Xie, L.; Ge, R.; Kong, R.; Liu, Z.; Du, G.; Asiri, A. M.; Yao, Y.; Luo, Y. Core-Shell NiFe-LDH@ NiFe-Bi Nanoarray: In Situ Electrochemical Surface Derivation Preparation toward Efficient Water Oxidation Electrocatalysis in near-Neutral Media. ACS Appl. Mater. Interfaces 2017, 9 (23), 19502–19506.

(15) Liu, P.-F.; Zhou, J.-J.; Li, G.-C.; Wu, M.-K.; Tao, K.; Yi, F.-Y.; Zhao, W.-N.; Han, L. A hierarchical NiO/NiMn-layered double hydroxide nanosheet array on Ni foam for high performance supercapacitors. *Dalt. Trans.* **201**7, *46* (23), 7388–7391.

(16) Stern, L.-A.; Hu, X. Enhanced oxygen evolution activity by NiO_x and Ni (OH)₂ nanoparticles. *Faraday Discuss.* **2014**, 176, 363–379.

(17) Tian, T.; Jiang, J.; Ai, L. In situ electrochemically generated composite-type CoO_x/WO_x in self-activated cobalt tungstate nanostructures: implication for highly enhanced electrocatalytic oxygen evolution. *Electrochim. Acta* **2017**, *224*, 551–560.

(18) Feng, J.; Xu, H.; Dong, Y.; Ye, S.; Tong, Y.; Li, G. FeOOH/Co/ FeOOH Hybrid Nanotube Arrays as High-Performance Electrocatalysts for the Oxygen Evolution Reaction. *Angew. Chem.* **2016**, *128*, 3758–3762.

(19) Feng, J.; Ye, S.; Xu, H.; Tong, Y.; Li, G. Design and Synthesis of FeOOH/CeO 2 Heterolayered Nanotube Electrocatalysts for the Oxygen Evolution Reaction. *Adv. Mater.* **2016**, *28*, 4698–4703.

(20) Lu, X.; Gu, L.; Wang, J.; Wu, J.; Liao, P.; Li, G. Bimetal-Organic Framework Derived CoFe2O4/C Porous Hybrid Nanorod Arrays as High-Performance Electrocatalysts for Oxygen Evolution Reaction. *Adv. Mater.* 2017, 29, 1604437.

(21) Ye, S.; Shi, Z.; Feng, J.; Tong, Y.; Li, G. Activating CoOOH Porous Nanosheet Arrays by Partial Iron Substitution for Efficient Oxygen Evolution Reaction. *Angew. Chem., Int. Ed.* **2018**, *57*, 2672– 2676.

(22) Karthick, K.; Anantharaj, S.; Karthik, P. E.; Subramanian, B.; Kundu, S. Self-Assembled Molecular Hybrids of CoS-DNA for Enhanced Water Oxidation with Low Cobalt Content. *Inorg. Chem.* **2017**, *56*, 6734–6745.

(23) Chen, J. S.; Ren, J.; Shalom, M.; Fellinger, T.; Antonietti, M. Stainless steel mesh-supported NiS nanosheet array as highly efficient catalyst for oxygen evolution reaction. *ACS Appl. Mater. Interfaces* **2016**, *8*, 5509–5516.

(24) Wang, D. Y.; Gong, M.; Chou, H. L.; Pan, C. J.; Chen, H. A.; Wu, Y.; Lin, M. C.; Guan, M.; Yang, J.; Chen, C. W.; Wang, Y. L.; Hwang, B. J.; Chen, C. C.; Dai, H. Highly Active and Stable Hybrid Catalyst of Cobalt-Doped FeS₂ Nanosheets-Carbon Nanotubes for Hydrogen Evolution Reaction. *J. Am. Chem. Soc.* **2015**, *137*, 1587– 1592.

(25) Zhao, X.; Zhang, H.; Yan, Y.; Cao, J.; Li, X.; Zhou, S.; Peng, Z.; Zeng, J. Engineering the Electrical Conductivity of Lamellar Silver-Doped Cobalt (II) Selenide Nanobelts for Enhanced Oxygen Evolution. *Angew. Chem., Int. Ed.* **2017**, *56*, 328–332.

(26) Zhang, C.; Xin, B.; Duan, S.; Jiang, A.; Zhang, B.; Li, Z.; Hao, J. Controllable 1D and 2D Cobalt Oxide and Cobalt Selenide Nanostructures as Highly Efficient Electrocatalysts for the Oxygen Evolution Reaction. *Chem. - Asian J.* **2018**, *13*, 2700–2707.

(27) Carim, A. I.; Saadi, F. H.; Soriaga, M. P.; Lewis, N. S. Electrocatalysis of the hydrogen-evolution reaction by electrodeposited amorphous cobalt selenide films. *J. Mater. Chem. A* **2014**, *2*, 13835–13839.

(28) Zhang, J. Y.; Lv, L.; Tian, Y.; Li, Z.; Ao, X.; Lan, Y.; Jiang, J.; Wang, C. Rational Design of Cobalt-Iron Selenides for Highly Efficient Electrochemical Water Oxidation. *ACS Appl. Mater. Interfaces* **2017**, *9*, 33833–33840.

(29) Li, S.; Peng, S.; Huang, L.; Cui, X.; Al-Enizi, A. M.; Zheng, G. Carbon-Coated Co³⁺-Rich Cobalt Selenide Derived from ZIF-67 for Efficient Electrochemical Water Oxidation. *ACS Appl. Mater. Interfaces* **2016**, *8*, 20534–20539.

(30) Masud, J.; Swesi, A. T.; Liyanage, W. P. R.; Nath, M. Cobalt Selenide Nanostructures: An Efficient Bifunctional Catalyst with High Current Density at Low Coverage. *ACS Appl. Mater. Interfaces* **2016**, *8*, 17292–17302.

(31) Wang, Z.; Li, J.; Tian, X.; Wang, X.; Yu, Y.; Owusu, K. A.; He, L.; Mai, L. Porous Nickel-Iron Selenide Nanosheets as Highly Efficient Electrocatalysts for Oxygen Evolution Reaction. *ACS Appl. Mater. Interfaces* **2016**, *8*, 19386–19392.

(32) Swesi, A. T.; Masud, J.; Liyanage, W. P. R.; Umapathi, S.; Bohannan, E.; Medvedeva, J.; Nath, M. Textured NiSe2 Film: Bifunctional Electrocatalyst for Full Water Splitting at Remarkably Low Overpotential with High Energy Efficiency. *Sci. Rep.* **2017**, *7*, 1– 11.

(33) Liu, B.; Zhao, Y. F.; Peng, H. Q.; Zhang, Z. Y.; Sit, C. K.; Yuen, M. F.; Zhang, T. R.; Lee, C. S.; Zhang, W. J. Nickel–Cobalt Diselenide 3D Mesoporous Nanosheet Networks Supported on Ni Foam: An All-pH Highly Efficient Integrated Electrocatalyst for Hydrogen Evolution. *Adv. Mater.* **2017**, *29*, 1606521.

(34) Liao, M.; Zeng, G.; Luo, T.; Jin, Z.; Wang, Y.; Kou, X.; Xiao, D. Three-dimensional coral-like cobalt selenide as an advanced electrocatalyst for highly efficient oxygen evolution reaction. *Electrochim. Acta* **2016**, *194*, 59–66.

(35) Xia, C.; Liang, H.; Zhu, J.; Schwingenschlögl, U.; Alshareef, H. N. Active Edge Sites Engineering in Nickel Cobalt Selenide Solid Solutions for Highly Efficient Hydrogen Evolution. *Adv. Energy Mater.* **2017**, *7*, 1–9.

(36) Xia, C.; Jiang, Q.; Zhao, C.; Hedhili, M. N.; Alshareef, H. N. Selenide-Based Electrocatalysts and Scaffolds for Water Oxidation Applications. *Adv. Mater.* **2016**, *28*, 77–85.

(37) Panda, C.; Menezes, P. W.; Walter, C.; Yao, S.; Miehlich, M. E.; Gutkin, V.; Meyer, K.; Driess, M. From aMolecular 2Fe-2SePrecursor to aHighly EfficientIron Diselenide Electrocatalyst for Overall Water Splitting. *Angew. Chem., Int. Ed.* **2017**, *56*, 10506–10510.

(38) Zhu, J.; Ni, Y. Phase-controlled synthesis and the phasedependent HER and OER performances of nickel selenide nanosheets prepared by an electrochemical deposition route. *CrystEngComm* **2018**, 20, 3344–3352.

(39) Li, X.; Zhang, L.; Huang, M.; Wang, S.; Li, X.; Zhu, H. Cobalt and nickel selenide nanowalls anchored on graphene as bifunctional electrocatalysts for overall water splitting. *J. Mater. Chem. A* **2016**, *4*, 14789–14795.

(40) Xu, X.; Du, P.; Chen, Z.; Huang, M. An electrodeposited cobalt-selenide-based film as an efficient bifunctional electrocatalyst for full water splitting. *J. Mater. Chem. A* **2016**, *4*, 10933–10939.

(41) Hou, Y.; Lohe, M. R.; Zhang, J.; Liu, S.; Zhuang, X.; Feng, X. Vertically oriented cobalt selenide/NiFe layered- double-hydroxide nanosheets supported on exfoliated graphene foil: an efficient 3D electrode for overall water splitting. *Energy Environ. Sci.* **2016**, *9*, 478–483.

(42) Swesi, A. T.; Masud, J.; Nath, M. Nickel selenide as a highefficiency catalyst for oxygen evolution reaction. *Energy Environ. Sci.* **2016**, *9*, 1771–1782.

(43) Kong, D.; Wang, H.; Lu, Z.; Cui, Y. CoSe₂ Nanoparticles Grown on Carbon Fiber Paper: An Efficient and Stable Electrocatalyst for Hydrogen Evolution Reaction. *J. Am. Chem. Soc.* **2014**, *136*, 4897–4900.

(44) Liu, T.; Liu, Q.; Asiri, A. M.; Luo, Y.; Sun, X. An amorphous CoSe film behaves as an active and stable full water-splitting electrocatalyst under strongly alkaline conditions. *Chem. Commun.* **2015**, *51*, 16683–16686.

(45) Anantharaj, S.; Amarnath, T. S.; Subhashini, E.; Chatterjee, S.; Swaathini, K. C.; Karthick, K.; Kundu, S. Shrinking the Hydrogen Overpotential of Cu by 1 V Imparting Ultralow Charge Transfer Resistance for Enhanced H_2 Evolution. *ACS Catal.* **2018**, *8*, 5686–5697.

(46) Kuzuya, A.; Ohya, Y. DNA nanostructures as scaffolds for metal nanoparticles. *Polym. J.* **2012**, *44*, 452–460.

(47) Goodman, C. M.; Chari, N. S.; Han, G.; Hong, R.; Ghosh, P.; Rotello, V. M. DNA-binding by functionalized gold nanoparticles: mechanism and structural requirements. *Chem. Biol. Drug Des.* **2006**, *67*, 297–304.

(48) Chen, Z.; Liu, C.; Cao, F.; Ren, J.; Qu, X. DNA metallization: principles, methods, structures, and applications. *Chem. Soc. Rev.* **2018**, *47*, 4017–4072.

(49) Karthick, K.; Anantharaj, S.; Kundu, S. Nickelo-Sulfurization of DNA Leads to an Efficient Alkaline Water Oxidation Electrocatalyst with Low Ni Quantity. *ACS Sustainable Chem. Eng.* **2018**, *6*, 6802–6810.

(50) Shi, Y.; Zhang, B. Recent advances in transition metal phosphide nanomaterials: synthesis and applications in hydrogen evolution reaction. *Chem. Soc. Rev.* **2016**, *45*, 1529–1541.

(51) Xu, J.; Li, J.; Xiong, D.; Zhang, B.; Liu, Y.; Wu, K. H.; Amorim, I.; Li, W.; Liu, L. Trends in activity for the oxygen evolution reaction on transition metal (M= Fe, Co, Ni) phosphide pre-catalysts. *Chem. Sci.* **2018**, *9*, 3470–3476.

(52) Anantharaj, S.; Karthik, P. E.; Kundu, S. Self-assembled IrO_2 nanoparticles on a DNA scaffold with enhanced catalytic and oxygen evolution reaction (OER) activities. *J. Mater. Chem. A* **2015**, *3*, 24463–24478.

(53) Anantharaj, S.; Ede, S. R.; Karthick, K.; Sam Sankar, S.; Sangeetha, K.; Karthik, P. E.; Kundu, S. Precision and Correctness in the Evaluation of Electrocatalytic Water Splitting: Revisiting Activity Parameters with a Critical Assessment. *Energy Environ. Sci.* **2018**, *11*, 744–771.

(54) Li, Y.; Qiu, W.; Qin, F.; Fang, H.; Hadjiev, V. G.; Litvinov, D.; Bao, J. Identification of Cobalt Oxides with Raman Scattering and Fourier TransformTransform Infrared Spectroscopy. *J. Phys. Chem. C* **2016**, *120*, 4511–4516.

(55) Yu, B.; Qi, F.; Chen, Y.; Wang, X.; Zheng, B.; Zhang, W.; Li, Y.; Zhang, L. C. Nanocrystalline $Co_{0.85}$ Se Anchored on Graphene Nanosheets as a Highly Efficient and Stable Electrocatalyst for Hydrogen Evolution Reaction. *ACS Appl. Mater. Interfaces* **2017**, *9*, 30703–30710.