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Back-illuminated Si based photoanode with nickel cobalt oxide catalytic protection layer

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Abstract: Si is an excellent photoabsorber for use in dual band gap photoelectrochemical water splitting. We investigate photoanodes with n⁺pp⁺-Si configuration under back-side illumination which is suited to work in a tandem device stack. A co-sputtered NiCoO_x film coupled to the Si was used as a protective catalyst for the water oxidation reaction in 1M KOH. The sample showed high photocurrent (21 mA cm⁻²) under the red-light (38.6 mW cm⁻²). Long-term stability test showed gradual decrease of activity in the beginning, and then the activity was increased, yielding a cathodic shift of the onset voltage (> 50 mV) likely due to divergent response of Ni and Co to Fe present in KOH. Once the activity of the sample is stabilized, no further degradation was observed for the following 60 days, indicating that the demonstrated back-illuminated photoanode configuration can be considered as a promising architecture to be applied as a bottom cell of the tandem water splitting device under alkaline conditions.

Introduction

For efficient hydrogen (H₂) production via water splitting reaction, both hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) need to proceed with a high-rate.^[1,2] However, the kinetically slow OER process has been a major bottleneck,^[3] since it comprises several intermediate steps with high activation energy barriers and thus requires a high overpotential (η) to transfer the 4 electrons: 2H₂O → 4H⁺ + O₂ + 4e⁻ (in acid) or 4OH⁻ → 2H₂O + O₂ + 4e⁻ (in alkaline). To overcome this problem, efficient OER catalysts are required, but the state of the art electrocatalysts for OER, such as IrO₂ and RuO₂,^[4-6] are precious metal oxides and too expensive to scale-up, despite of their excellent OER activity in acidic media. In this context, earth-abundant transition metal oxides have been intensively investigated to develop cost-effective alternative OER materials with high activity.^[7,8] As one of the non-noble catalyst for OER, nickel cobalt oxide

(hereinafter NiCoO_x) has recently attracted considerable attention, despite the fact that it is stable only in alkaline media, mainly because of its excellent electrical conductivity and rich redox kinetics due to the large number of active sites.^[9] Compared to elemental oxides, such as NiO and Co₃O₄, NiCoO_x is promising candidate for applications, such as electrocatalytic anodic oxygen evolution, supercapacitors, sensors, or optical limiters and switches.^[9-12] Similarly in recent studies^[13,14] Fe modified NiO compounds have been demonstrated to be efficient OER catalysts. The Boettcher's group^[14] found that Fe enhances the film conductivity of nickel-based oxide, and claimed that incorporated Fe enhances the OER activity through a Ni-Fe partial charge transfer activation process, as has been proposed by Corrigan et al.^[15] Furthermore, this study also reported that the overpotential of Ni(OH)₂ film for OER can be reduced during cyclic voltammetry (CV) process in 1M KOH due to incorporation of trace amounts of Fe present in KOH.^[13] Thus, unintentional, but beneficial Fe alloying or doping occurs. So far, a number of approaches to obtain functional Ni-Fe-O compounds have been reported.^[13-16] Large-scale combinational screening studies^[17,18] have shown that not only Ni with Fe, but also other metallic elements (e.g., Co, Al, Ce) appear to enhance the OER-activity of Ni based oxides. These recent studies indicate that various combinations of cations provide the possibility to change the electrochemical properties. At the same time, it also implies that the OER activity of NiCoO_x would be also enhanced simply by aging in the electrolyte without any intentional doping procedure.

To date, many research groups have demonstrated catalytic behavior of element nickel or cobalt oxides^[16,19-24] while a relatively small number of studies report the electrocatalytic activity of the binary nickel-cobalt oxides.^[9-11] In the present work we demonstrate the time-dependant behavior of the OER kinetics of NiCoO_x thin films in 1M KOH (pH = 14) electrolyte. The NiCoO_x with Co interlayer is deposited by DC-sputtering on p⁺pn⁺ Si photoelectrodes, and we evaluate the OER kinetic variation of the sample as a function of the operating time under back side illumination. According to the Pourbaix diagrams, both nickel and cobalt oxide can be converted to hydroxides during potential cycling in alkaline electrolyte,^[25,26] and both materials have been used as a protection layer of Si photoabsorbers with frontal illumination.^[16,19,22,23] However, in actual tandem device operation conditions a low band gap absorber, such as Si, should be used as bottom cell of the tandem water splitting device, where the light is incident from the "dry"

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side of the photoanode. We have demonstrated successful hydrogen production using a light-permeable ring-shaped Al back contact under back-illumination condition,^[27] and this approach is also employed in this study to allow illumination from the side opposing the solid/liquid interface (i.e. NiCoO_x side). Since the photons are irradiated from the back contact side, transparency of the protection layer is not a required property, indicating that thick, non-transparent protection layers can be employed.

10 Results and Discussion

11 The p-type c-Si with a shallow n⁺p-junction at the side opposing the solid/liquid interface was coupled with a 50-nm-thick NiCoO_x protective OER catalyst. The NiCoO_x was deposited by co-sputtering of Ni and Co with same deposition rate (i.e. Ni:Co ≈ 15 1:1) under oxygen flow. The back side of the samples was covered with a quartz glass to protect back side from direct contact with the electrolyte as shown in Figure 1a. The Co interlayer was introduced to prevent oxidation of the Si surface during the metal oxide deposition, and to provide an efficient pathway for the carrier injection by forming an Ohmic contact as shown in energy band diagram (Figure 1b).

22 Scanning electron microscopy (SEM) images of the NiCoO_x with Co interlayer deposited on a Si substrate are shown in Figure 2. Figure 2a and b correspond to cross-sectional and top-view image of the film, respectively. The cross-sectional SEM image indicates that the NiCoO_x film is continuous above the Si substrate and has a thickness of about 50 nm, and thus the surface is covered completely. This also can be found from the top-view SEM image (Figure 2b) exposing a dense NiCoO_x surface without any obvious cracks or pin-holes. Note that the investigated films were deposited on the Si photoelectrodes using the same conditions as those used for the PEC samples, and the presence of nickel and cobalt in the binary oxide layer

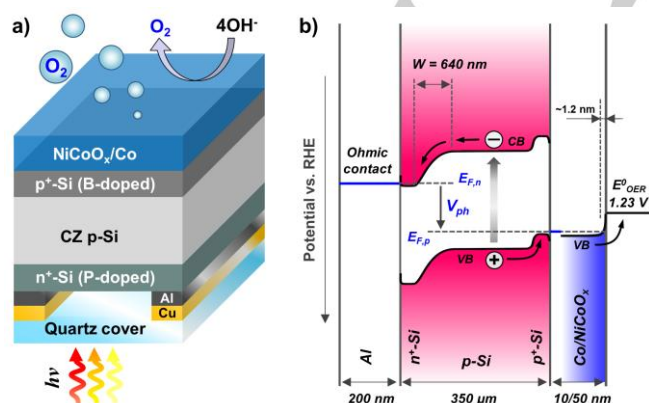


Figure 1. (a) Schematic drawing of the back illuminated photoanode with Al/n⁺pp⁺-Si/Co/NiCoO_x (NiCoO_x on top) and (b) band alignment under illumination. Energy diagram calculation procedure can be found in Supporting Information.

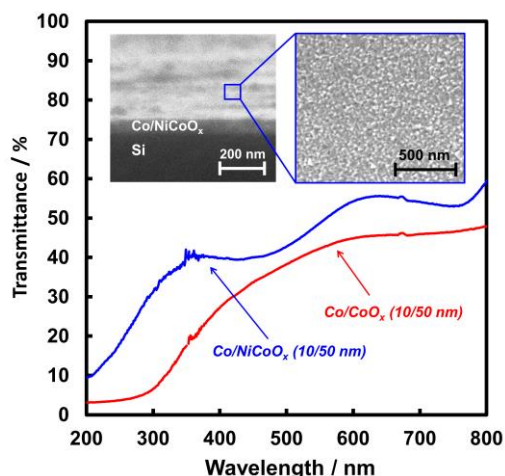


Figure 2. UV-Vis transmittance spectra of NiCoO_x (blue) and CoO_x (red) deposited on quartz substrate with Co interlayer. The signal from the quartz substrate was subtracted as a background spectrum. Cross-sectional SEM image of n⁺pp⁺Si/Co/NiCoO_x and top-view SEM image are also shown as inset. The NiCoO_x film was deposited at 300°C, and these SEM images well demonstrate excellent surface coverage without any obvious cracks or pinholes.

34 was confirmed by energy dispersive X-ray spectroscopy (EDX) analysis (Figure S1 in Supporting Information). The optical behavior of the deposited films was investigated by UV-Vis transmittance spectroscopy as shown in Figure 2. Transmittance of deposited NiCoO_x was only approximately 53% at 600 nm in wavelength in spite of its wide band-gap over 2.75 eV.^[28] As shown in our recent work^[15] a NiO thin film with 50 nm thickness shows over 80% transmittance at 600 nm wavelength due to its high band gap (3.5 ~ 3.6 eV), and thus the optical loss of Co/NiCoO_x would partially due to the Co interlayer. However, a Co/CoO_x layer with same thickness shows transmittance of 43% at the same wavelength having a band-gap of around 1.96 ~ 2.36 eV,^[29] and it is suggested that the optical loss and decreased band gap of NiCoO_x can be mainly attributed to the mixed cobalt oxide phase which shows a drastic increase of absorption coefficient with increased growth temperature.^[30] This illustrates how back illumination is beneficial for photoanodes based on such overlayers.

52 NiCoO_x is a well-known p-type, mixed-valence oxide with Ni occupying octahedral sites and Co distributed over both octahedral and tetrahedral sites.^[31] To confirm the conductivity type of the present NiCoO_x thin film, electrochemical impedance measurements were performed (i.e. Mott-Schottky analysis). The resulting Mott-Schottky plot (Figure S2) shows a negative slope, confirming the p-type behavior of the deposited NiCoO_x films. The flat band potential (E_{FB}) and the acceptor density (N_A) were estimated to be $E_{FB} \approx 0.7$ V versus RHE and $N_A \approx 7 \cdot 10^{18}$ cm⁻³, respectively, and this high dopant density should provide sufficient conductivity to transport holes through the valence band.

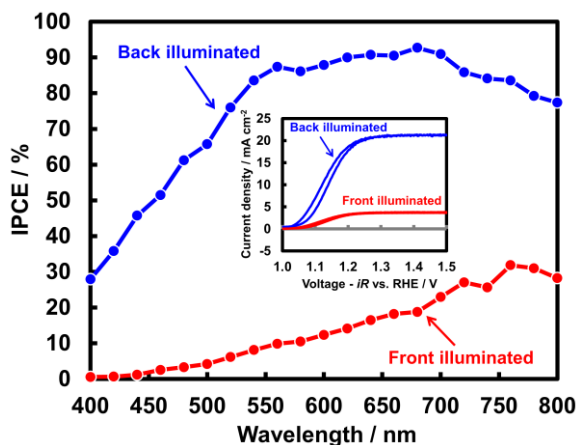


Figure 3. IPCE measurement results under front and back-illumination using $n^{+}pp^{+}Si/Co/NiCoO_x$ photoanode sample, and the inset is cyclic voltammetry scans under front and back side illumination (AM 1.5G and 635 nm cut-off filters were used in the cyclic voltammetry scans). Note that imperfect active-area definition by epoxy encased electrodes can cause an overrating of IPCE.

1 To verify the photoelectrochemical properties of $NiCoO_x$, this film
 2 was coupled with the $n^{+}pp^{+}Si$ photoanode with a Co interlayer
 3 between the $p^{+}Si$ and $NiCoO_x$ regions, and the sample was
 4 examined by CV and incident photon to current efficiency (IPCE)
 5 measurements. The difference between the overpotentials η
 6 required to obtain a 10 mA cm^{-2} with the $p^{+}Si/Co/NiCoO_x$ (under
 7 dark) and $n^{+}pp^{+}Si/Co/NiCoO_x$ (38.6 mW cm^{-2} under the back
 8 illumination) reveals a photovoltage (V_{ph}) of $\sim 510\text{ mV}$ (Figure
 9 S3), which is in good agreement with the V_{ph} determined for our
 10 previous $p^{+}pn^{+}Si$ photocathode with Pt catalyst under same light
 11 spectrum condition.^[27]

12 Figure 3 shows spectrally resolved IPCE measurement results
 13 of the $n^{+}pp^{+}Si/Co/NiCoO_x$ photoanode under back side and
 14 front side illumination. Each data point was measured at an
 15 applied bias of 1.4 V vs. RHE , at which the sample shows a
 16 saturated photocurrent for both front and back side illumination.
 17 As shown in Figure 3, the IPCE under the back side illumination
 18 increases gradually and shows IPCE close to 85% at 550 nm for
 19 photons, which are absorbed near the back side of the sample.
 20 Considering the light absorption depth of Si as a function of the
 21 wavelength,^[27] this high IPCE response is natural since the
 22 charge collecting pn-junction is placed at the back side of the
 23 sample, and this shows that this $n^{+}pp^{+}Si/Co/NiCoO_x$ structure is
 24 an efficient configuration to be used as a bottom cell of the
 25 tandem device. The low IPCE response in the short wavelength
 26 range ($\sim 500\text{ nm}$) is mainly attributed to the high recombination
 27 rate at the $n^{+}Si$ surface. Note that we did not apply any surface
 28 passivation treatment, and there is no significant optical loss due
 29 to the quartz cover glass in this wavelength range.^[27]
 30 Conversely, the IPCE of the same sample under front side
 31 illumination increases slowly from the short wavelength region
 32 and reaches merely 30% at a wavelength of 800 nm because
 33 most of the electron-hole pairs are generated far from the pn-
 34 junction under the front illumination, and due to the poor
 35 transmittance of the $NiCoO_x$ layer as shown in Figure 2. Note

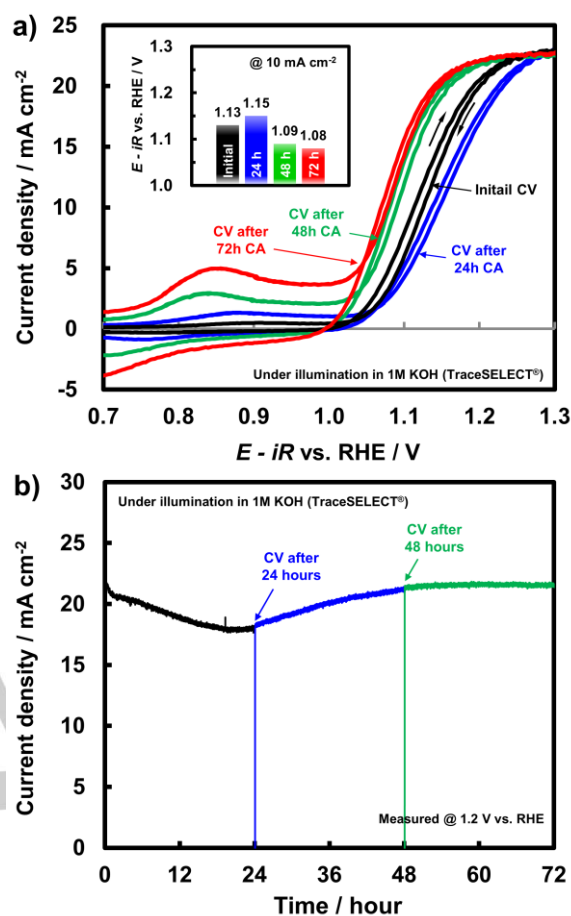


Figure 4. (a) Cyclic voltammograms of $n^{+}pp^{+}Si/Co/NiCoO_x$ photoanode measured before chronoamperometry measurement (black), after the 24 hours long chronoamperometry (blue), after the 48 hours (green), and after the 72 hours long chronoamperometry (red). (b) CA measurements carried out at 1.2 V vs. RHE . The potentials required to achieve a photocurrent density of 10 mA cm^{-2} measured every 24 hours can be found in inset of 4a.

36 that imperfect active-area definition by epoxy (Loctite 1C Hysol)
 37 encased electrodes can cause an overrating of IPCE^[32], but not
 38 affect on the qualitative behavior. This difference in IPCE
 39 behavior between the front and back side illumination is
 40 reflected in the CV measurement results (inset in Figure 3). The
 41 saturated photocurrent of the $n^{+}pp^{+}Si/Co/NiCoO_x$ photoanode
 42 sample is around 21 mA cm^{-2} under the back side illumination
 43 with approximate AM 1.5G + 635 nm long pass filters, whereas
 44 significantly lower photocurrent, less than 5 mA cm^{-2} was
 45 measured under front illumination.

46 In order to investigate time-dependant behavior of the sample,
 47 repeated CV measurements with long-term chronoamperometry
 48 (CA) measurements were carried out. As shown in Figure 4a,
 49 the potential required to achieve a photocurrent density (J_{ph}) of
 50 10 mA cm^{-2} was found to depend on the operating time. An
 51 applied potential of 1.13 V was required for the initial CV curve.
 52 This performance compares well our previous study with an as-
 53 deposited NiO , which showed relatively gradual slope, requiring
 54 an applied potential of $\sim 1.24\text{ V}$ to reach the 10 mA cm^{-2}

1 benchmark^[16] This enhanced performance of NiCoO_x is in good
 2 agreement with that from the previous electrochemical study on
 3 as-deposited Ni-Co-O OER catalyst.^[10] Addition of Co, which
 4 abounds in the spinel structure of nickel oxide, is known to
 5 provide more active sites, and reduce intrinsic electrical
 6 resistivity.^[9,33] Tseung and Jasem^[34] suggested that the mixed
 7 valences of the nickel and cobalt cations are helpful in the
 8 reversible adsorption of oxygen by providing donor-acceptor
 9 sites for chemisorption, thus lowering the overpotential. Such
 10 synergetic effects are not limited to Ni-Co oxides, for instance
 11 recent studies on Ni-Fe-O oxides^[13,14] can be understood in the
 12 same context. Nevertheless, 1.18 V (at 10 mA cm⁻²) was
 13 required for the CV measured after 24 hours
 14 chronoamperometry test at 1.2 V, reflecting the changes in OER
 15 kinetics. These CV curves (initial and 24h after) showed a
 16 similar saturation current J_{ph} (~ 22 mA cm⁻²), but they behaved
 17 differently. Compared with the initial CV curve, the curve taken
 18 after 24 hours had an anodic shift of 20 mV at 10 mA cm⁻² and a
 19 decreased slope resulting a significant loss at the maximum
 20 power point (lower fill factor), which can result in significant loss
 21 of operating current density in tandem devices^[35] and can be
 22 attributed to the NiCoO_x catalyst layer. The anodic shift
 23 accompanying with the decreased slope might be explained by
 24 the reaction of Co-O compounds with the alkaline electrolyte.
 25 Boettcher's group reported in their recent work that ppb-level
 26 iron impurities in KOH electrolyte substitute for Co³⁺ under the
 27 applied potential, and this substitution incorporation decreases
 28 the electrical conductivity of the CoOOH phase,^[36] and our ICP-
 29 MS analysis revealed Fe of approximately 30 ppb in the
 30 electrolyte. In this report, the reduced conductivity appears as a
 31 lowered the fill factor (i.e. decreased slope in CV curve). Since
 32 our photoanode sample with sputtered CoO_x showed a
 33 continuous anodic shift of onset potential with decreased fill
 34 factor, this resulted in an increase in overpotential of
 35 approximately 40 mV after 3 days operation (Figure S4). This is
 36 in agreement with the recent report by the Lewis' group that the
 37 CoO_x coupled with a Si photoanode shows a gradual loss in
 38 catalytic activity associated with the conversion of CoO_x to
 39 Co(OH)₂ and then to ion-permeable cobalt oxyhydroxide
 40 (CoOOH).^[22]

41 Interestingly, the required bias potential to reach 10 mA cm⁻²
 42 rebounded in the cathodic direction after the first 24 hours and
 43 reached 1.07 V vs. RHE after the 3 days of chronoamperometry
 44 measurement. Furthermore, the slope of CV curves increased
 45 sharply compared to that of the CV curve taken right after the
 46 first 24 hours. Since the photoanode with Co/CoO_x showed a
 47 continuous anodic shift of onset voltage as well as degradation
 48 in photocurrent, it appears reasonable to assume that the
 49 increased activity is mainly attributed to the incorporation of Fe³⁺
 50 with Ni²⁺. A number of recent studies^[13,14,16] have revealed that
 51 the apparent OER activity of NiO is dramatically affected by
 52 small amounts of Fe impurities in alkaline electrolyte, causing a
 53 cathodic shift in the OER onset potential. The increased redox
 54 peak in Figure 4a also implies a strong interaction of Fe with

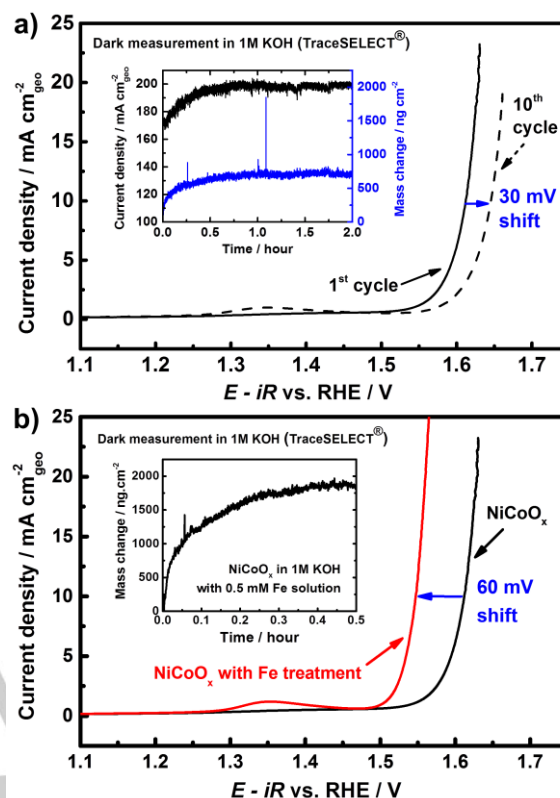


Figure 5. (a) Electrochemical cyclic voltammetry measurement result for the NiCoO_x deposited on EQCM sample with Co interlayer with subsequent 2 hours long chronoamperometry and mass change measurement data (inset), and (b) electrochemical current-potential of NiCoO_x before (black) and after Fe-treatment (red). Both chronoamperometry and mass change measurements were carried out with fixed applied potential of 1.8 V vs. RHE using EQCM's.

55 metal sites, such as Co and/or Ni. The integrated area under the
 56 redox feature yields the total charge exchanged between the
 57 incorporated ions and the active sites of the electrode,^[37] and
 58 thus the increased redox features shown in Figure 4a may
 59 indicate that a significant number of metallic sites have become
 60 electrochemically accessible. The redox wave peak of the
 61 oxidative current slightly shifted cathodically for the CV curves
 62 taken after 24h and 48h relative to that of the initial CV curve,
 63 then anodically shifted toward the OER current peak. The later
 64 anodic shift of the redox wave is well known for the binary metal
 65 oxides, i.e. CoO_x and NiO. This anodic redox wave shift
 66 observed in Figure 4a is consistent with the previous
 67 reports,^[13,36] where the redox wave for Co^{2+/3+} and Ni^{2+/3+} shifts
 68 anodically as the Fe content in the oxide films increases.

69 However, only few studies reported the presence of the negative
 70 shift of redox peak. J. M. Marioli et al.^[38] observed that this
 71 negative shift takes place for the Ni-Cr binary oxide films,
 72 whereas single component nickel oxide showed only anodic
 73 redox peak shift. S. Kim et al. also reported^[39] that the shifts in
 74 the Ni^{2+/3+} redox features in the negative direction (> 50 mV) is
 75 induced by the presence of Co in the Ni hydrous oxide lattice. In
 76 agreement with the previous observations by other

1 groups,^[10,38,39] no discernible voltammetry features associated
 2 with the $\text{Co}^{2+}/\text{Co}^{3+}$ redox couple can be identified for the composite
 3 Ni-Co oxide film. Despite of a harmony with previous
 4 observations, the precise effect on the catalytic mechanism
 5 remains unknown.

6 The CA study performed at 1.2 V versus RHE for 3 days (Figure
 7 4b) reflects the above mentioned behavior of CV curves. At a
 8 fixed potential of 1.2 V vs. RHE, the J_{ph} of the n^+pp^-
 9 Si/Co/NiCoO_x dropped quite quickly from around 22 to 20.5 mA
 10 cm^{-2} over about half an hour, after which photocurrent output
 11 appears to degrade slowly with constant rate. This degradation
 12 continued during the first 20 hours of CA measurement, followed
 13 by a slow increase in J_{ph} after ~ 22 hours followed by a stabilized
 14 J_{ph} from the 3rd day of the CA experiment. Once the J_{ph}
 15 saturated, the sample showed stable J_{ph} output until 144th hours
 16 (6 days) without any further changes or degradation (Figure S5).

17 Assuming that incorporation rate or diffusion rate of Fe thought
 18 the ion-permeable oxyhydroxide structures is independent of
 19 time, these CV and CA behaviors are interesting. They suggest
 20 that Fe incorporation in the beginning is insufficient to lead to
 21 increased activity, but sufficient to lead to decreased activity due
 22 to the iron incorporated cobalt oxyhydroxide components.
 23 Subsequently the Fe incorporation becomes sufficient to cause
 24 an improved OER activity after a certain point. It was found that
 25 this V-shape of the Si photoanode with Co/NiCoO_x is
 26 reproducible, as confined by an additional CA experiment using
 27 a new, but similar, sample showed the same time-dependent
 28 behavior (see Figure S6).

29 The electrochemical properties of NiCoO_x thin film deposited on
 30 electrochemical quartz crystal microbalance (EQCM) sample
 31 were investigated by means of CV and CA in 1 M KOH
 32 (TraceSelect) under dark condition (Figure 5). The as-deposited
 33 NiCoO_x films (Figure 5, black trace) show quite good
 34 performance for the OER. An overpotential of ~ 380 mV is
 35 required to achieve a current density of 10 mA cm^{-2} which is in
 36 good agreement with the overpotentials obtained in the
 37 photoelectrochemical tests (Figure 4a). Nevertheless, after 10
 38 cycles the potential at 10 mA cm^{-2} is shifted anodically by 30
 39 mV. The anodic shift closely resembles the drop in current
 40 density in the long-term stability PEC tests and the
 41 corresponding anodic shift of the CV curves (Figure 4a).
 42 Subsequent 2 hours long CA measurement (Figure 5a inset)
 43 showed increase in current density along with mass change
 44 during the first 0.5 hours. Afterwards, the NiCoO_x thin film
 45 deposited on EQCM was intentionally doped with Fe (Figure 5b,
 46 NiCoO_x in KOH with 0.5 mM Fe) according to a procedure
 47 previously used for NiO thin films.^[16] The EQCM result (Figure
 48 5b inset) shows a significant increase in mass during treatment
 49 of NiO in a Fe-containing solution, which was found to be
 50 saturated after ~ 0.5 h of treatment. This behavior is similar to
 51 mass change for as-deposited NiCoO_x in Figure 5a. We attribute
 52 this increase in mass at least partially to Fe incorporation
 53 occurring in parallel with oxygen evolution. Interestingly, in the

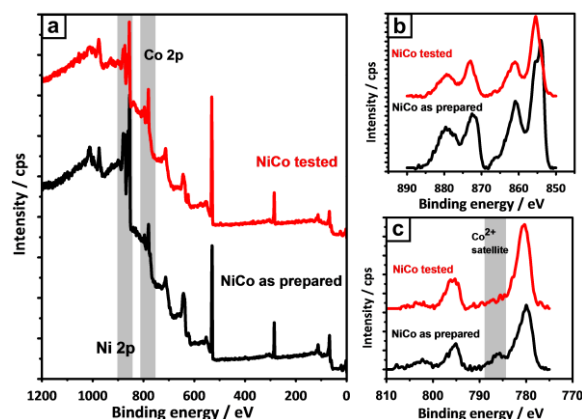


Figure 6. (a) XPS survey spectra of the NiCoO_x thin film deposited on EQCM substrate with Co interlayer, and zoomed in (b) Ni 2p XPS spectra, (c) Co 2p region. Black and red color correspond to the curve for the as prepared and after the electrochemical test, respectively.

54 subsequently performed CV measurement (Figure 5b) a
 55 cathodic shift of 60 mV compared to the as-prepared NiCoO_x
 56 thin film was observed. Thus, an overpotential of ~ 320 mV was
 57 required to obtain a current density of 10 mA cm^{-2} . This
 58 enhanced performance of the Fe-doped NiCoO_x thin film is in
 59 good agreement with the enhancement during prolonged CA of
 60 the NiCoO_x thin film used for the back-illuminated PEC studies
 61 and can therefore be attributed to a self-driven enhancement of
 62 nickel cobalt oxide by metallic Fe-contamination during
 63 photoelectrochemical oxygen evolution reaction. To further
 64 investigate on this, X-ray photoelectron spectroscopy (XPS) was
 65 performed. XPS measurements were performed on as-prepared
 66 NiCoO_x thin films (prepared on EQCM substrates) and on
 67 NiCoO_x thin films after 24h of continuous operation at a potential
 68 of 1.8 V vs. RHE. Detailed scans of the Ni 2p and Co 2p regions
 69 derived from the survey spectra in Figure 6a are included in
 70 Figure 6b and 6c. The as prepared NiCoO_x thin film consists of a
 71 mixture of $\text{Ni}^{2+}/\text{Ni}^{3+}$ (at binding energies of 854/856 eV) and
 72 $\text{Co}^{2+}/\text{Co}^{3+}$ (suggested by the satellite feature at 785 eV). After
 73 continuous testing for 24 h XPS measurements reveal that Ni
 74 and Co are mainly present in their 3+ oxidation state (binding
 75 energy of 856 eV for Ni^{3+} shown in Figure 6b. For Co^{3+} a
 76 characteristic binding energy of 780.5 eV was measured.
 77 Furthermore, the characteristic Co^{2+} satellite signal at 785 eV
 78 was significantly reduced as shown in Figure 6c). The presence
 79 of different oxidation states in the as-prepared NiCoO_x thin film
 80 as well as its further oxidation during prolonged testing is in
 81 good agreement with previously reported NiO thin films prepared
 82 and tested under similar conditions^[16] and can be ascribed to the
 83 transformation into its more porous NiOOH and CoOOH
 84 oxidation states which act as hosts for Fe-impurities.^[19,36]
 85 Binding energy increase of O1s peak (Figure S7) for the tested
 86 sample is also support the formation of the oxyhydroxide
 87 phase.^[40] The direct detection of Fe by means of XPS was not
 88 possible in this case due to the Al source's strong overlap with
 89 Ni LMM Auger signal and the unfavorable Fe cross section.
 90 Using Mg Ka source, which was not available for the XPS used

1 in this work, would allow detection of trace Fe. However, the
2 transformations into more open NiOOH and CoOOH in the
3 NiCoO_x thin film accompanied with the presented data of NiCoO_x
4 studied on EQCM substrate strongly suggest the self-driven
5 enhancement of nickel cobalt oxide by metallic Fe-contamination
6 during prolonged photoelectrochemical oxygen evolution
7 reaction. In addition, Ni and Fe distribution mapped by EDX
8 (Figure S7) of the porous NiCoO_x deposited on the Si
9 photoanode after 6 days of CA testing at 1.2 V versus RHE also
10 directly supports the presence of Fe, along with above
11 mentioned EQCM results.

12 Conclusions

13 A back-illuminated n⁺pp⁺-Si has been coupled to earth-
14 abundant Ni-Co based catalysts and investigated as
15 photoanode for the oxygen evolution reaction. Specifically
16 we have demonstrated the performance of a n⁺pp⁺-
17 Si/Co/NiCoO_x structure, whose pn-junction is formed at the
18 side opposing the solid/liquid interface, may efficiently drive
19 the OER under back side (dry side) illumination which will
20 be the actual operational condition in a tandem water
21 splitting device. Importantly, taking advantage of the
22 synergetic effects between Ni and Co, the NiCoO_x OER
23 catalyst coating exhibits excellent catalytic activity as well
24 as long-term stability in highly concentrated alkaline media,
25 which makes it a strong candidate for the practical OER
26 catalysts. Interestingly, the photoanode samples activated
27 by NiCoO_x show a non-trivial time-dependent current-
28 voltage behavior in OER activity. In 1M KOH the sample
29 studied initially exhibits an anodic shift of onset potential,
30 followed by a rebound in the cathodic direction which is
31 likely due to Fe incorporation into Ni-Co oxyhydroxide which
32 acts as a host for Fe incorporation. This work highlights an
33 approach to using a low band gap photoanode in actual
34 tandem device operation condition, and enhancing its
35 photocatalytic activity by simple aging process.

36 Experimental Section

37 Sample fabrication

38 The shallow n⁺p-junction was produced in p-type (100) czochralski (CZ)
39 Si wafers (Topsil, 1-20 ohm-cm, boron-doped) by a shallow phosphorous
40 ion implantation at 36 keV with a dose of 3×10¹⁵ cm⁻². After annealing a
41 mesa-isolated n⁺p-Si structure with height of 3 μm is formed at the back
42 side (light illumination side) by photolithography and dry etching (Here,
43 we used Ar, O₂ and CHF₃ gases in an Oxford Instruments RIE80). The
44 front side of the same samples was also doped with boron doping using
45 ion implantation at 100 keV with a dose of 5×10¹⁶ cm⁻² to form a thin p⁺
46 layer. An Al charge collecting layer with a circular hole for light irradiation
47 was deposited by e-beam evaporation with a metallic shadow mask to
48 make circular rings for light irradiation. More fabrication details also can
49 be found in our previous work^[27] and Supporting Information.

50 Prior to the deposition of the NiCoO_x protective OER catalyst, the Si was
51 sputtered in Ar to clean the surface and remove the native oxide.
52 Subsequently, a 10 nm Co metallic film was reactively sputtered in 3
53 mTorr of pure Ar followed by the deposition of 50 nm of NiCoO_x in 3
54 mTorr at an O₂/Ar ratio of 40% by co-sputtering of Ni and Co targets with
55 same deposition rate (i.e. Ni:Co ≈ 1:1). In case of EQCM and glass
56 substrates, Co/NiCoO_x thin films were deposited using the same process
57 conditions as mentioned above. Samples prepared only with cobalt oxide
58 (Co/CoO_x) are used to verify qualitatively the role of the Ni component in
59 the binary oxide layer during the reaction. The back side of the samples
60 was covered with a 300 μm thick quartz glass, and was mounted directly
61 onto the Al layer. The resulting active area after covering with epoxy was
62 measured by image analysis using ImageJ 1.46r after the experiments.
63 Schematic cross-sectional configuration and its energy band diagram are
64 shown in Figure 1, and a more detailed description of the related
65 calculation procedure also can be found in Supporting Information.

66 Characterization

67 Photoanodes consisting of n⁺pp⁺Si/Co/NiCoO_x were evaluated under
68 back-side illumination using a 1000 W Xenon lamp (Oriel) with AM 1.5g
69 and 635 nm cut-off filters to appropriately approximate the wavelengths
70 and intensity that this electrode would receive in a practical tandem water
71 splitting device. All CV and chronoamperometry experiments were done
72 in a 3 electrode quartz cell, since intensive corrosion of conventional
73 pyrex can poison or cover the active surface with glass corrosion
74 products,^[41] and consequently hinder the light absorption. All (photo)
75 electrochemical measurements were performed in high-purity aqueous 1
76 M KOH (Aldrich, TraceSELECT[®], ≥ 99.995%) using a Bio-Logic VSP
77 potentiostat with EC Lab software. A Pt mesh was used as a counter
78 electrode and the reference was a saturated Hg/HgO electrode (Koslow
79 Scientific Company). The detailed experimental setup and procedure are
80 provided in the Supporting Information. The solution was purged with Ar
81 gas 30 minutes prior to any experiment. Inductively coupled plasma
82 mass spectrometry (ICP-MS) experiments were performed (Thermo
83 Fisher Scientific, iCAP-QC) for the quantification of iron impurity in the
84 electrolyte.

85 To determine efficiency as a function of wavelength, IPCE
86 measurements were employed. An Oriel 74100 monochromator was
87 combined with the Xenon lamp mentioned above to give monochromatic
88 light. IPCE measurements were carried out from 400 to 800 nm under
89 both front side and back side illumination. To confirm the conductivity
90 type of the present NiCoO_x thin film, electrochemical impedance
91 measurements were performed (Mott-Schottky plot analysis) under the
92 dark condition. Both IPCE and Mott-Schottky analyses were carried out
93 using same equipment and setup as that used for CV measurements.

94 The results in the present work also cover the electrochemical stability of
95 the NiCoO_x film, and therefore, emphasis also has been put on
96 electrochemical measurements using EQCM samples under the dark
97 conditions to monitor the mass change that occurs during the
98 electrochemical reaction. For this purpose, a three electrode setup
99 similar to that of photocatalytic CV and CA measurements was used. The
100 EQCM measurements were performed with a 5 MHz QCM200 supplied
101 by Stanford Research Systems.

102 In order to determine the structural properties, XPS analysis was carried
103 out in an UHV (ultra-high vacuum) system provided by Thermo Scientific.
104 In this work, an Al Kα X-ray source emitting photons with energy 1486.7
105 eV has been used.

106 SEM with EDX was also carried out for the surface morphology and
107 cross-sectional investigations using Quanta FEG SEM. The provided
108 electron beam energy was 5 to 20 kV with a working distance of around

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1 10 cm. The transmittance spectra were recorded using a Varian Cary 1E
2 UV-Vis Spectrophotometer to estimate band-gap and optical absorption
3 of the deposited Co/NiCoO_x (NiCoO_x on top) and Co/CoO_x layers on
4 quartz substrate. To avoid the effect of background signal, including the
5 absorption by the substrate and/or light scattering particulates in the
6 instrument, a baseline correction using a bare quartz substrate has been
7 carried out prior to the measurements for the NiCoO_x and CoO_x
8 deposited samples.

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13 **Keywords:** oxygen evolution, nickel cobalt oxide, water splitting,
14 solar fuel, photocatalysis

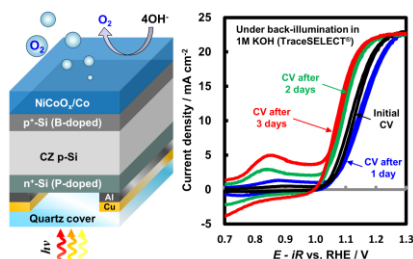
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Layout 1:

FULL PAPER

Binary metal oxide under back-illumination: crystalline Si (c-Si) coupled with a thin layer of NiCoO_x is applied as a photoanode for water oxidation under back-side illumination to be used as a bottom cell of the tandem water splitting device. The thin layer of NiCoO_x effectively protects c-Si from the alkaline electrolyte for 6 days under oxygen evolution reaction.



*Dowon Bae, Bastian Mei, Rasmus Fryndendal, Thomas Pedersen, Brian Seger, Ole Hasen, Peter C. K. Vesborg, Ib Chorkendorff**

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Back-illuminated Si based photoanode with nickel cobalt oxide catalytic protection layer

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