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Published in:
ChemElectroChem

Link to article, DOI:
10.1002/celc.201500554

Publication date:
2016

Document Version
Peer reviewed version

Link back to DTU Orbit

Citation (APA):
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 photovoltaic/photocatalytic conversion processes. We have developed a tandem device, consisting of a NiCoO catalyst layer and a p-type Si substrate illuminated from the back. A co-sputtered NiCoO film was deposited on the Si, coupled to a TiO2 electron acceptor layer. The film was used as the photoanode in a 1 M KOH electrolyte. The film stability was shown to be high and the activity was increased, yielding a cathodic photocurrent of 21.1 mA cm\(^{-2}\) under red-light illumination (38.6 mW cm\(^{-2}\)). The observed photocurrent density was stable for more than 50 mV, likely due to a high electrocatalytic activity of NiCoO. The activity of NiCoO could be increased by aging the film, and the activity was further increased by Fe alloying or doping. This opens the possibility to increase the overall water splitting efficiency by using a tandem device with NiCoO as the photoanode and an Fe alloy as the photovoltaic material. The present study confirms the high potential of NiCoO as a high performance OER catalyst for dual band gap conversion processes.

Introduction

For efficient hydrogen (H\(_2\)) production via water splitting, 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,\(^{[4]}\) and thus requires a high overpotential (\(\eta\)) to transfer 4 electrons: \(2\text{H}_2\text{O} \rightarrow 4\text{H}^+ + 4\text{e}^-\) (in acid) or \(4\text{OH}^- \rightarrow 2\text{H}_2\text{O} + 4\text{e}^-\) (in alkaline). To overcome this problem, efficient OER catalysts are required, but the state of the art catalysts for OER, such as \(\text{IrO}_2\) and \(\text{RuO}_2\),\(^{[5,6]}\) 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.\(^{[7,8]}\) Among one of the non-noble catalyst for OER, nickel cobalt oxide \((\text{NiCoO})\) 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 \(\text{NiO}\) and \(\text{Co}_3\text{O}_4\), \(\text{NiCoO}\) 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 \(\text{NiO}\) compounds have been demonstrated to be efficient OER catalysts. The Boettcher’s group\(^{[16]}\) found that Fe enhances the film conductivity of nickel-based oxide, and incorporated that 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 \(\text{Ni(OH)}_2\) film for OER can be reduced during cyclic voltammetry (CV) process in 1 M 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 combinatorial 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 \(\text{NiCoO}\) 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\(^{[16,19-24]}\), and 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-dependent behavior of the OER kinetics of \(\text{NiCoO}\) thin films in 1 M KOH (pH = 14) electrolyte. The \(\text{NiCoO}\), with Co interlayer is deposited by DC-sputtering on p⁺ pn⁺ Si photodelectrodes, 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 oxides 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 photoanodes with front 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”...
side of the photoanode. We have demonstrated successful hydrogen production using a light-permeable ring-shaped Al back contact under back-illumination condition, and this approach is also employed in this study to allow illumination from the side opposing the solid/liquid interface (i.e. NiCoO$_2$ 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.

**Results and Discussion**

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$_2$ protective OER catalyst. The NiCoO$_2$ was deposited by co-sputtering of Ni and Co with same deposition rate (i.e. Ni:Co = 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).

Scanning electron microscopy (SEM) images of the NiCoO$_2$ 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$_2$ 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$_2$ 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 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$_2$ was only approximately 53% at 600 nm in wavelength in spite of its wide band-gap over 2.75 eV. As shown in our recent work 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$_2$, would partially due to the Co interlayer. However, a Co/NiCoO$_2$ layer with same thickness shows transmittance of 43% at the same wavelength having a band-gap of around 1.96 - 2.36 eV, and it is suggested that the optical loss and decreased band gap of NiCoO$_2$ can be mainly attributed to the mixed cobalt oxide phase which shows a drastic increase of absorption coefficient with increased growth temperature. This illustrates how back illumination is beneficial for photoanodes based on such overlayers.

NiCoO$_2$ is a well-known p-type, mixed-valence oxide with Ni occupying octahedral sites and Co distributed over both octahedral and tetrahedral sites. To confirm the conductivity type of the present NiCoO$_2$ 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$_2$ films. The flat band potential ($E_{FB}$) and the acceptor density ($N_a$) were estimated to be $E_{FB} = 0.7$ V versus RHE and $N_a = 7 \times 10^{16}$ cm$^{-3}$, respectively, and this high dopant density should provide sufficient conductivity to transport holes through the valence band.
To verify the photoelectrochemical properties of NiCoO\(_x\), this film was coupled with the n\(^{-}\)p\(^{+}\)-Si photonoade with a Co interlayer between the p\(^{-}\)-Si and NiCoO\(_x\) regions, and the sample was examined by CV and incident photon to current efficiency (IPCE) measurements. The difference between the overpotentials \(\eta\) required to obtain a 10 mA cm\(^{-2}\) with the p\(^{+}\)-Si/NiCoO\(_x\)-(under dark) and n\(^{-}\)p\(^{+}\)-Si/NiCoO\(_x\) (38.6 mW cm\(^{-2}\) under the back illumination) reveals a photovoltage (\(V_{ph}\)) of \(\sim 510\) mV (Figure S3), which is in good agreement with the \(V_{ph}\) determined for our previous p\(^{+}\)n\(^{-}\) Si photonoade with Pt catalyst under same light spectrum condition.\(^{[27]}\)

Figure 3 shows spectrally resolved IPCE measurement results of the n\(^{-}\)p\(^{+}\)-Si/NiCoO\(_x\) photonoade under back side and front side illumination. Each data point was measured at an applied bias of 1.4 V vs. RHE, at which the sample shows a saturated photocurrent for both front and back side illumination.\(^{[7]}\)

As shown in Figure 3, the IPCE under the back side illumination increases gradually and shows IPCE close to 85% at 550 nm for photons, which are absorbed near the back side of the sample. Considering the light absorption depth of Si as a function of the wavelength,\(^{[27]}\) this high IPCE response is natural since the charge collecting pn-junction is placed at the back side of the sample, and this shows that this n\(^{-}\)p\(^{+}\)-Si/NiCoO\(_x\) structure is an efficient configuration to be used as a bottom cell of the tandem device. The low IPCE response in the short wavelength range (\(\sim 500\) nm) is mainly attributed to the high recombination rate at the n\(^{-}\)-Si surface. Note that we did not apply any surface passivation treatment, and there is no significant optical loss due to the quartz cover glass in this wavelength range.\(^{[27]}\)

Conversely, the IPCE of the same sample under front side illumination increases slowly from the ‘short wavelength region and reaches merely 30% at a wavelength of 800 nm because most of the electron-hole pairs are generated far from the pn-junction under the front illumination, and due to the poor transmittance of the NiCoO\(_x\) layer as shown in Figure 2. Note that imperfect active-area definition by epoxy (Loctite 1C Hysol) encased electrodes can cause a overrating of IPCE.\(^{[32]}\)

\(\eta\) = \(E - IR\) vs. RHE / V

\(E = IR\) vs. RHE / V

This performance compares well our previous study with an as-deposited NiO, which showed relatively gradual slope, requiring an applied potential of \(\sim 1.24\) V to reach the 10 mA cm\(^{-2}\) under front side illumination.\(^{[12]}\)

In order to investigate time-dependant behavior of the sample, repeated CV measurements with long-term chronoamperometry (CA) measurements were carried out. As shown in Figure 4a, the potential required to achieve a photocurrent density \(J_{ph}\) of 10 mA cm\(^{-2}\) was found to depend on the operating time. An applied potential of 1.13 V was required for the initial CV curve. This performance compares well our previous study with an as-deposited NiO, which showed relatively gradual slope, requiring an applied potential of \(\sim 1.24\) V to reach the 10 mA cm\(^{-2}\) under front side illumination.\(^{[12]}\)
This enhanced performance of NiCoO$_x$ is in good agreement with that from the previous electrochemical study on as-deposited Ni-Co-O OER catalyst.\textsuperscript{[10]} Addition of Co, which abounds in the spinel structure of nickel oxide, is known to provide more active sites, and reduce intrinsic electrical resistivity.\textsuperscript{[22,23]} Tseung and Jasem\textsuperscript{[30]} suggested that the mixed valences of the nickel and cobalt cations are helpful in the reversible adsorption of oxygen by providing donor-acceptor sites for chemiabsorption, thus lowering the overpotential. Such synergetic effects are not limited to Ni-Co oxides, for instance recent studies on Ni-Fe-O oxides\textsuperscript{[13,14]} can be understood in the same context. Nevertheless, 1.18 V (at 10 mA cm$^{-2}$) was required for the CV measured after 24 hours chronoamperometry test at 1.2 V, reflecting the changes in OER kinetics. These CV curves (initial and 24th after) showed a similar saturation current $I_{on}$ (~ 22 mA cm$^{-2}$), but they behaved differently. Compared with the initial CV curve, the curve taken after 24 hours had an anodic shift of 20 mV at 10 mA cm$^{-2}$ and a decreased slope resulting a significant loss at the maximum power point (lower fill factor), which can result in significant loss of operating current density in tandem devices\textsuperscript{[35]} and can be attributed to the NiCoO$_x$ catalyst layer. The anodic shift accompanying with the decreased slope might be explained by the reaction of Co-O compounds with the alkaline electrolyte. Boettcher’s group reported in their recent work that ppb-level iron impurities in KOH electrolyte substitute for Co$^{3+}$ in the applied potential, and this substitution incorporation decreases the electrical conductivity of the CoOOH phase.\textsuperscript{[36]} and our ICP-MS analysis revealed Fe of approximately 30 ppb in the electrolyte. In this report, the reduced conductivity appears as a lowered the fill factor (i.e. decreased slope in CV curve). Since our photoanode sample with sputtered Co$_x$O$_y$ showed a continuous anodic shift of onset potential with decreased fill factor, this resulted in an increase in overpotential of approximately 40 mV after 3 days operation (Figure S4). This is in agreement with the recent report by the Lewis’ group that the Co$_x$O$_y$ coupled with a Si photoanode shows a gradual loss in catalytic activity associated with the conversion of Co$_x$O$_y$ to Cr$_x$(OH)$_y$ and then to ion-permeable cobalt oxyhydroxide (CoOOH).\textsuperscript{[36]}

Interestingly, the required bias potential to reach 10 mA cm$^{-2}$ rebounded in the cathodic direction after the first 24 hours and reached 1.07 V vs. RHE after the 3 days of chronoamperometry measurement. Furthermore, the slope of CV curves increased sharply compared to that of the CV curve taken right after the first 24 hours. Since the photoanode with Co$_x$O$_y$Co$_x$O$_y$ showed a continuous anodic shift of onset voltage as well as degradation in photocurrent, it appears reasonable to assume that the increased activity is mainly attributed to the incorporation of Fe$^{3+}$ with Ni$^{2+}$. A number of recent studies\textsuperscript{[13,14,16]} have revealed that the apparent OER activity of NiO is dramatically affected by small amounts of Fe impurities in alkaline electrolyte, causing a cathodic shift in the OER onset potential. The increased redox peak in Figure 4a also implies a strong interaction of Fe with metal sites, such as Co and/or Ni. The integrated area under the redox feature yields the total charge exchanged between the incorporated ions and the active sites of the electrode.\textsuperscript{[37]} and thus the increased redox features shown in Figure 4a may indicate that a significant number of metallic sites have become electrochemically accessible. The redox wave peak of the oxidative current slightly shifted cathodically for the CV curves taken after 24h and 48h relative to that of the initial CV curve, and then anodically shifted toward the OER current peak. The later anodic shift of the redox wave is well known for the binary metal oxides, i.e. CoO and NiO. This anodic redox wave shift observed in Figure 4a is consistent with the previous reports,\textsuperscript{[13,36]} where the redox wave for Co$^{3+}$/$^2+$ and Ni$^{3+}$/$^2+$ shifts anodically as the Fe content in the oxide films increases. However, only few studies reported the presence of the negative shift of redox peak. J. M. Marioli et al.\textsuperscript{[38]} observed that this negative shift takes place for the Ni-Cr binary oxide films, whereas single component nickel oxide showed only anodic redox peak shift. S. Kim et al. also reported\textsuperscript{[39]} that the shifts in the Ni$^{3+}$/$^2+$ redox features in the negative direction (> 50 mV) is induced by the presence of Co in the Ni hydroxide oxide lattice. In agreement with the previous observations by other

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.

This is the pre-peer reviewed version of the following article: Bae, D et al., \textit{Back-Illuminated Si-Based Photoanode with Nickel Cobalt Oxide Catalytic Protection Layer}. ChemElectroChem, which has been published in final form at doi:10.1002/celc.201500554. This article may be used for non-commercial purposes in accordance with Wiley Terms and Conditions for Self-Archiving.
groups, no discernible voltammetry features associated with the Co\(^{2+/3+}\) redox couple can be identified for the composite Ni-Co oxide film. Despite of a harmony with previous observations, the precise effect on the catalytic mechanism remains unknown.

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

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

The electrochemical properties of NiCoO\(_x\) thin film deposited on electrochemical quartz crystal microbalance (EQCM) sample investigated by means of CV and CA in 1 M KOH (TraceSelect) under dark condition (Figure 5). The as-deposited NiCoO\(_x\) films (Figure 5, black trace) show quite good performance for the OER. An overpotential of ~380 mV is required to achieve a current density of 10 mA cm\(^{-2}\) which is in good agreement with the overpotentials obtained in the photoelectrochemical test (Figure 4a). Nevertheless, after 10 cycles the potential at 10 mA cm\(^{-2}\) is shifted anodically by 30 mV. The anodic shift closely resembles the drop in current density in the long-term stability PEC tests and the corresponding anodic shift of the CV curves (Figure 4a).

Subsequent 2 hours long CA measurement (Figure 5a inset) showed increase in current density along with mass change during the first 0.5 hours. Afterwards, the NiCoO\(_x\) thin film deposited on EQCM was intentionally doped with Fe (Figure 5b, NiCoO\(_x\) in KOH with 0.5 mM Fe) according to a procedure previously used for NiO thin films.\(^{[16]}\) The EQCM result (Figure 5b inset) shows a significant increase in mass during treatment of NiO in a Fe-containing solution, which was found to be saturated after ~0.5 h of treatment. This behavior is similar to mass change for as-deposited NiCoO\(_x\) in Figure 5a. We attribute this increase in mass at least partially to Fe incorporation occurring in parallel with oxygen evolution. Interestingly, in the subsequent performed CV measurement (Figure 5b) a cathodic shift of 60 mV compared to the as-prepared NiCoO\(_x\) thin film was observed. Thus, an overpotential of ~320 mV was required to obtain a current density of 10 mA cm\(^{-2}\). This enhanced performance of the Fe-doped NiCoO\(_x\) film is in good agreement with the enhancement during prolonged CA of the NiCoO\(_x\) thin film used for the back-illuminated PEC studies and can therefore be attributed to a self-driven enhancement of nickel cobalt oxide by metallic Fe-contamination during photoelectrochemical oxygen evolution reaction. To further investigate on this, X-ray photoelectron spectroscopy (XPS) was performed. XPS measurements were performed on as-prepared NiCoO\(_x\) thin films (prepared on EQCM substrates) and on NiCoO\(_x\) thin films after 24 h of continuous operation at a potential of 1.8 V vs. RHE. Detailed scans of the Ni 2p and Co 2p regions derived from the survey spectra in Figure 6a are included in Figure 6b and 6c. The as-prepared NiCoO\(_x\) thin film consists of a mixture of Ni\(^{2+/3+}\)/Ni\(^{3+}\) (at binding energies of 854/856 eV) and Co\(^{2+/3+}\) (suggested by the satellite feature at 785 eV). After continuous testing for 24 h XPS measurements reveal that Ni and Co are mainly present in their 3\(^{+}\) oxidation state (binding energy of 856 eV for Ni\(^{3+}\) shown in Figure 6b. For Co\(^{3+}\) a characteristic binding energy of 780.5 eV was measured. Furthermore, the characteristic Co\(^{2+}\) satellite signal at 785 eV was significantly reduced as shown in Figure 6c). The presence of different oxidation states in the as-prepared NiCoO\(_x\) thin film as well as its further oxidation during prolonged testing is in good agreement with previously reported NiO thin films prepared and tested under similar conditions\(^{[16]}\) and can be ascribed to the transformation into its more porous NiOOH and CoOOH oxidation states which act as hosts for Fe-impurities.\(^{[19,36]}\) Binding energy increase of O1s peak (Figure S7) for the tested sample is also support the formation of the oxyhydroxide phase.\(^{[40]}\) The direct detection of Fe by means of XPS was not possible in this case due to the Al source’s strong overlap with Ni LMM Auger signal and the unfavorable Fe cross section. Using Mg K\(\alpha\) 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 thin film accompanied with the presented data of NiCoO 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, 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"p"-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"p"- 17 Si/Co/NiCoO 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, 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+ 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) czechralski (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 3x10^17 cm^-2. After annealing a 41 mess-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 5x10^18 cm^-2 to form a thin p" layer. An Al charge collecting layer with a circular hole for light irradiation 46 was deposited by e-beam evaporation with a metallic shadow mask to 47 make circular rings for light irradiation. More fabrication details also can 48 be found in our previous work[27] and Supporting Information.

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

65 Characterization

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

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

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

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

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 109 the sample thickness.
Acknowledgements

This work was performed as a part of the Center for Individual Nanoparticle Functionality (CINF) which is funded by Danish National Research Foundation (DNRF54).

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

Binary metal oxide under back-illumination: crystalline Si (c-Si) coupled with a thin layer of NiCoOₓ 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 NiCoOₓ effectively protects c-Si from the alkaline electrolyte for 6 days under oxygen evolution reaction.

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