One-step preparation of optically transparent Ni-Fe oxide film electrocatalyst for oxygen evolution reaction

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ABSTRACT

Optically transparent cocatalyst film materials is very desirable for improved photoelectrochemical (PEC) oxygen evolution reaction (OER) over light harvesting photoelectrodes which require the exciting light to irradiate through the cocatalyst side, i.e., front-side illumination. In view of the reaction overpotential at electrode/electrolyte interface, the OER electrocatalysts have been extensively used as cocatalysts for PEC water oxidation on photoanode. In this work, the feasibility of a one-step fabrication of the transparent thin film catalyst for efficient electrochemical OER is investigated. The Ni-Fe bimetal oxide films, ~200 nm in thickness, are used for study. Using a reactive magnetron co-sputtering technique, transparent (> 50% in wavelength range 500–2000 nm) Ni-Fe oxide films with high electrocatalytic activities were successfully prepared at room temperature. Upon optimization, the as-prepared bimetal oxide film with atomic ratio of Fe/Ni = 3:7 demonstrates the lowest overpotential for the OER in aqueous KOH solution, as low as 329 mV at current density of 2 mA cm⁻², which is 135 and 108 mV lower than that of as-sputtered FeO_x and NiO_x thin films, respectively. It appears that this fabrication strategy is very promising to deposit optically transparent cocatalyst films on photoabsorbers for efficient PEC water splitting.

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1. Introduction

Photoinduced water splitting reaction to produce hydrogen is regarded as one of the cleanest and the most promising ways for capturing and storing the inexhaustible energy from the sun [1–3]. Photoelectrochemical (PEC) strategy based on semiconductor photoelectrode, as first reported by Fujishima and Honda [4], has received considerable attention and been studied extensively as a promising method for over four decades [5–11]. However, the energy conversion efficiency and operational stability of the

material (photoelectrode) are needed to substantially improve for sustainable hydrogen production by PEC water splitting in future [12]. To improve the catalytic performance of photoelectrodes, cocatalyst thin films are often deposited on the semiconducting photoabsorber for fabrication of composite photoelectrode (demonstrated structure in Fig. 1). The cocatalysts can be employed to passivate surface defects [13], to isolate electrolyte [14], or in most cases to facilitate the photoelectrode/electrolyte interface charge transfer process [15–20], especially for the dynamically sluggish oxygen evolution reaction (OER) on the photoanode.

The film thickness of cocatalyst overlayer has been indicated as an important factor for improved PEC performance of composite photoelectrodes, and particularly crucial when the exciting light is irradiated through the cocatalyst side, i.e., front-side illumination as shown in Fig. 1. For example, surface modification of Co-Pi overcoating with thickness <~ 10 nm on meso-structured α-Fe₂O₃ is beneficial to photocurrent enhancement and beyond which

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deleterious instead [18,19]; thin metallic nickel films (2–5 nm) on n-type Si photoanode raises photocurrent saturation level, while the thicker (10–30 nm) do exactly oppositely [13]. The reason is attributed to parasitic photon absorption by the cocatalysts themselves, introducing new absorption losses with increasing overcoating thickness. To avoid light absorption interference, the illumination direction is altered to through the optical transparent conductive substrate (generally FTO or ITO glass), i.e., backside illumination as shown in Fig. 1. In this case, the optimal cocatalyst film thickness is dramatically increased. For instance, the photocurrent for water oxidation reaction over planar α -Fe₂O₃ continuously elevates with increasing Co-Pi overlayer thickness up to 425 nm [21]. However, a variety of important semiconducting photoanodes, including conventional crystalline Si and newly developed metal (oxy) nitrides, have to be fabricated on non-transparent conductive substrates (generally metal or carbon paper), for the reason of preparation requirements such as high temperature processing. Thus, it is very desirable to develop optically transparent cocatalyst films for photoelectrodes that require front-side illumination for improved PEC performance.

As the OER is a complicated process involving a four-proton coupled four-electron transfer, it is very challenging to achieve efficient water photoelectrolysis and water electrolysis. In view of the reaction overpotential at electrode/electrolyte interface, the OER electrocatalysts have been extensively used as cocatalysts for PEC water oxidation on photoanode [15–20]. While by far, the most active OER electrocatalysts are RuO₂ [22] and IrO₂ [23], their scarcity and high cost make them impractical to use on a large scale [24,25]. Being earth-abundant, low-cost and environmentally benign, the Ni–Fe bimetallic systems, including NiFe₂O₄ [26], Ni–Fe layered double hydroxide [27] and Ni–Fe oxides [28,29], are found to be promising OER electrocatalysts. In particular, the electrodeposited Ni–Fe oxide film is regarded as an outstanding alternative for precious metal catalysts [24,30]. In addition, Ni–Fe oxide film catalyst shows satisfying durability in oxygen-enriched environment [28,29]. Besides electrodeposition technique, evaporation-induced self-assembly [31], polymer precursor method [32], dip-coating [33–35] and reactive sputtering [36] have been established to prepare crystalline Ni–Fe oxide catalysts. However, amorphous phase of Ni–Fe oxides has seldom been reported [37]. Moreover, their optical properties have not been investigated.

Reactive magnetron sputtering has been widely used in preparing large area uniform thin films well adhered to the underlying substrates. The structure of the deposited film can be easily controlled by adjusting process parameters, and the process is reproducible. In particular, depositing cocatalyst layer over semiconductor photoelectrode by the clean vacuum method can be continuously operated in addition to protecting the substrate from erosion in solution process. Hence, the current technique has

Fig. 1. Schematic illustration of front- and backside illumination over composite photoelectrode.

Table 1

Experimental conditions for the as-prepared Ni–Fe oxide thin-films by direct current reactive magnetron co-sputtering technique.

Oxide films	Ni			Ni–Fe			Fe
Sample ID	Ni	NF1	NF2	NF3	NF4	NF5	Fe
Ni target Power (W)	200	200	200	200	150	100	0
Fe target Power (W)	0	50	150	200	300	350	350
Deposition Time (min.)	30	30	25	20	12	12	15
Thickness (nm)	200	200	210	200	220	220	200
Fe (at.%) ^a	0	8.4	25.6	31.4	71.1	85.5	100

^a Data obtained from the XPS analysis.

potential for practical, large-scale manufacturing of the thin film cocatalyst materials for fabrication of composite photoelectrodes [38]. In fact, there have been a few metal oxide electrocatalysts, including nickel oxide [36], Ta–Ni oxide [39] and RuO_x [40], prepared using this method for electrochemical OER.

Herein, we report our development in using reactive magnetron co-sputtering to prepare Ni–Fe oxide thin-film catalysts at room temperature for the electrochemical OER in an aqueous KOH solution. The film thickness is set at 200 nm as a benchmark for this investigation. The obtained Ni–Fe oxide catalysts are amorphous and the optimal OER activity was achieved at Fe/Ni atomic ratio $\sim$ 3:7. The optical properties as well as electrochemical performance of the thin film catalysts for OER in alkaline electrolyte were investigated. To our best knowledge, this is the first report to prepare optically transparent Ni–Fe oxide thin film electrocatalysts for OER. A possible mechanism is proposed and discussed in detail.

2. Experimental

2.1. Preparation of thin films

The iron oxide, nickel oxide and Fe–Ni oxide films were deposited on FTO (NSG, sheet resistance of 20 Ω per square) glass substrates by direct current reactive magnetron co-sputtering technique using a sputtering machine (PVD 75, Kurt J. Lesker Company). The sputtering targets are iron and nickel metals with a purity of 99.99% (Φ 75 $\times$ 1 mm, Grikin Advanced Materials Co. Ltd.). The sputtering system was pumped using a turbo molecular pump

Fig. 2. XRD patterns of the investigated thin film deposited on the glass slide substrate.

Fig. 3. SEM images of the as-sputtered thin films deposited on FTO substrate.

backed with a mechanic pump. Before deposition, the chamber was evacuated to 1×10^{-3} Pa, and then high purity Ar and O₂ gases were introduced into the chamber. All gas flows were controlled by individual mass flow controllers. All depositions were conducted at 1 Pa and the oxygen: Ar ratio was kept at 30%. The target-substrate spacing was kept at 90 mm. No extra heating and biasing were applied for the substrate during or post deposition. The deposition time is regulated to achieve film thickness ~ 200 nm for all materials.

2.2. Physical Characterization

The morphology of the samples was examined by Scanning Electron Microscopy (SEM) using a Quanta 200FEG scanning electron microscope. The structure of the samples was studied by X-ray Diffraction (XRD) on a Rigaku D/Max-2500/PC powder diffractometer. The measurement was performed using CuK α as the radiation source with operating voltage 40 kV and current 200 mA. The scanning rate was kept at 5° min^{-1} with a step size 0.02° in the 2θ range of $20\text{--}70^\circ$. The UV-vis spectra were recorded on a spectrophotometer (JASCO V-550) equipped with an integrating sphere. The film thickness and the roughness were

measured using a Dektak 150 Surface Profiler, Veeco. X-ray Photoelectron Spectroscopy (XPS) was recorded on a Thermo Escalab 250 equipped with a monochromatic Al K α X-ray source. The spectra were analyzed using CasaXPS (Casa Software, Ltd.). A standard Shirley baseline without any offset was used for background correction. The C 1s spectrum for adventitious carbon (284.8 eV) was used for charge correction.

2.3. Electrochemical measurements.

Current density vs potential curves were recorded with a commercial potentiostat (CHI760D electrochemical workstation) and potential programmer, using a standard three-electrode system, with a Luggin capillary joining the reference electrode (RE) to the working electrode (WE) compartment, and a porous glass frit separating the WE and counter electrode (CE) compartments. A Pt foil and a saturated calomel electrode (SCE) were used as the CE and RE, respectively. The as-sputtered thin films on FTO substrates, as working electrodes, were prepared by attaching a copper wire on the edge of the FTO substrate using silver paste, followed by covering the surface with epoxy resin for insulation, except for an area of $0.5 \text{ cm} \times 0.5 \text{ cm}$ in the center. Electrochemical

Fig. 4. UV-vis transmittance spectra of Ni-Fe oxide thin films deposited on FTO substrates.

measurements were carried out in 0.1 M KOH aqueous solution. Without otherwise specified, the measured potentials vs SCE were converted to the RHE scale according to the Nernst equation ($E_{\text{RHE}} = E_{\text{SCE}} + 0.0591\text{pH} + 0.2415\text{V}$). Applied potential was linear swept from 1.1 to 1.9 V with a scanning rate of 5 mV s^{-1} . The relative electrochemical surface area (ECSA) was determined from capacitance measurements carried out by cyclic voltammetry in the region between -0.1 and 0 V vs. SCE in 0.1 M KOH aqueous solution, and the scan rates were varied between 25 and 250 mV s^{-1} . In all experiments, analytical grade chemicals were used without further purification. Water used was obtained by purifying deionized water with a Milli-Q water purification system.

3. Results and discussion

By controlling the sputtering power and deposition time, thin film samples at thickness of about 200 nm with different ratios of Fe/Ni are prepared on FTO substrate, as summarized in Table 1. For example, 30 min deposition at 200 W sputtering powers generates a $\sim 200\text{ nm}$ thick nickel oxide film. Co-sputtering the targets of iron at 50 W and nickel at 200 W for 30 min results in a composite thin film with 8.4% Fe. Keeping the sputtering power of nickel constant, at the same time elevating the sputtering power of iron to 150 and 200 W respectively in duration of 25 and 20 min, the obtained bimetal oxides correspondingly contain more iron up to 25.6% and 31.4%. In order to further increase the Fe/Ni ratio, the sputtering power for iron target is raised to 300 and 350 W with simultaneously decreased sputtering powers for nickel within a shorter deposition time as 12 min, the proportions of Fe are enhanced to 71.1 and 85.5%, respectively. The pure iron oxide thin film was also prepared for comparison. In the following discussion, the as-sputtered thin films are designated as Ni, NF x ($x = 1-5$) and Fe for pure nickel oxide, Ni-Fe oxides and pure iron oxide, respectively.

Fig. 2 shows XRD results of the samples. To avoid interference from the crystalline phases of the FTO substrate, the thin films were deposited on amorphous glass slides for the XRD measurement. It indicates that all thin films show an amorphous phase regardless of the Fe/Ni ratio. Miller et al. reported preparation of iron-doped nickel oxide by a similar method, while they harvested crystalline films [36]. Apart from the different process parameters for the reactive sputtering, the substrates were maintained at 50°C while no intentional heating or biasing was applied for our substrates during the film growth. It is probably understandable an amorphous phase is produced using such mild conditions. The surface morphologies of the thin film samples were observed using SEM (Fig. 3). All samples show compact surface morphology, similar to what shown in other films prepared using similar

magnetron sputtering technique [36,38–40]. All samples, including samples Ni, Fe, NF1 and NF2 with different Ni contents, show very similar appearance, while the small barbs on the surface of the aggregated particles disappear as the proportion of iron was increased to about 30–70% (Fig. 3d and 3e). The well connected particles with smooth surface were finally developed into plate-like morphology (Fig. 3f and 3g) when the ratio of Fe/Ni was further increased to 85% till the pure phase of iron oxide. To investigate the optical properties, the UV-vis transmittance spectra of the oxide film samples were measured and with results shown in Fig. 4. Obviously, in wavelength ranging from 500 to 2000 nm, the nickel oxide exhibits more light transmission than the iron oxide film. For this reason, nickel oxide films (thickness of 10–150 nm) have recently been applied as a protective layer on some self-passivating photoanodes, leading to a long duration over 100 hours in PEC oxidation of water to gas oxygen [41]. It should be noticed that the addition of iron impairs the transparency. However, there is over 50% of incident light in wavelength over 500 nm can pass through the Ni-Fe oxide films regardless of a large thickness up to 200 nm. In contrast, most incident light was blocked when a 30-nm-thick metal nickel layer or a 10-nm-thick cobalt phosphate electrocatalyst film was coated as a cocatalyst

Fig. 5. (a) Linear sweep voltammetric curves and (b) overpotentials for OER (at $j = 2, 5\text{ mA cm}^{-2}$) of the as-investigated Ni, NF1, NF2, NF3, NF4, NF5 and Fe thin films on FTO substrate. The inset is the onset potentials at 0.1 mA cm^{-2} for the investigated samples.

Fig. 6. XPS spectra of the as-sputtered Ni-Fe oxide and pure NiO_x and FeO_x film electrodes in the insets. (a) Ni 2p; (b) Fe 2p.

layer [13]. Moreover, reducing the thickness of the Ni-Fe oxide films is believed to further improve their optical transmittance. Thus, such optical transparent films are promising to be an excellent cocatalyst to a photoelectrode for enhanced PEC performance, in particular to semiconducting photoelectrode with wide visible light absorption typically over 500 nm in wavelength.

Electrochemical behavior of the as-sputtered Ni-Fe oxide thin film electrodes was measured using linear sweep voltammogram (LSV) in 0.1 M KOH aqueous solution (pH 13.0), as shown in Fig. 5a. The *j*-*V* curves of the single phase of amorphous iron oxide and nickel oxide electrodes are shown as references. The anodic current together with a large number of bubbles presented on the electrode surface shows that the oxygen gas evolved due to water oxidation reaction. The onset potential (at *j* = 0.1 mA cm⁻²) for OER of the investigated samples are listed in the inset in Fig. 5a. As

reported in previous results [28–37], the nickel oxide shows much higher electrocatalytic activity than the iron oxide thin film electrode. Once a small portion (< about 30%) of iron oxide was doped into or mixed with nickel oxide to form amorphous Ni-Fe oxides (sample NF1, NF2 and NF3), the onset potential for the OER negatively shifts by about 30–40 mV. While in the iron oxide dominated samples (NF4 and NF5), the onset potential rapidly shifts towards the positive direction to about 1.4 and 1.5 V, respectively. Consequently, the sample NF3 achieves the most negative current onset potential.

To better compare the electrocatalytic activity for OER, the overpotentials of the samples at the current density of 2 and 5 mA cm⁻² were estimated according to their LSV curves (Fig. 5a), as summarized in Fig. 5b. It is clearly shown that the addition of certain amount of Fe remarkably improves the electrochemical

Fig. 7. The linear relationship between the capacitive current and scan rate for the as-investigated electrodes. The inset is partial amplification for samples NF1, NF2, NF4 and NF5.

water splitting activity, in good agreement with previous reports [28–37]. The minimum overpotential was found at sample NF3 with Fe/Ni atomic ratio of 3:7, similar to 3:5 in the Geng's results on amorphous Ni-Fe- O_x catalysts obtained by an aerosol-spray-assisted approach [37]. The Tafel slope for sample NF3 was also obtained from the J-V plot using a linear fit applied to points in the Tafel region, resulting in a slope of ~ 123 mV/decade. In contrast, the previously amorphous Ni-Fe- O_x catalyst showed an optimal Tafel slope as low as ~ 48 mV/decade. A significant change in the Tafel slope is usually interpreted as a change in the rate-limiting step for the OER over different electrocatalytic materials [35]. According to the Krasil'shchikov theory on the reaction pathway for oxygen evolution in alkaline solutions [36], the primary discharge of OH^- ions is considered as rate limiting step on our NF3 catalyst exhibiting Tafel slope near 120 mV/dec; while the discharge of absorbed O^- species is the rate limiting step on Geng's catalysts. Further reason may be due to the difference on electrode morphology and the catalyst loading amount. Our sputter-deposited electrode has compact morphology (above SEM) in addition to low catalyst loading (thin film). In comparison, an aggregating nanoparticles appearance of Geng's catalyst evidently indicates a porous structure at a high loading amount. Additionally, at the current density 2 mA cm^{-2} , the overpotential for OER over sample NF3 is 329 mV, which is 108 and 135 mV lower than that of pure NiO_x and FeO_x electrodes, respectively. At a higher current density 5 mA cm^{-2} , the overpotential still keeps at a relatively low level at 384 mV on the NF3 electrode, while the overpotentials for the pure NiO_x and FeO_x are considerably higher at 519 and 668 mV, respectively.

Although beneficial effects of Fe on the electrochemical OER activity of Ni in alkaline electrolyte have been reported in a number of studies [25,42–45], little is known about the structural or chemical characteristics of crystalline Ni-Fe oxide catalysts, neither the amorphous phase. In this work, we used XPS to detect the surface atomic composition and the chemical shifts of Fe and Ni peaks. Fig. 6 shows XPS of a series of Fe-Ni oxide films and pure NiO_x or FeO_x as reference. In term of pure oxides, it is seen from the insets that two main peaks for Ni 2p locate at 854 and 873 eV for its $2p_{3/2}$ and $2p_{1/2}$ levels, and similarly two Fe 2p peaks locate at 710 and 723 eV for $2p_{3/2}$ and $2p_{1/2}$ levels. Meanwhile, the satellites peaks on the high energy side are clearly observed. From NF1 to NF5, the intensity for Fe element becomes increasingly stronger while that for Ni element becomes weaker and weaker, revealing composition change as listed in Table 1. In addition, quantifiable

chemical shifts in the binding energy are clearly observed for Ni-Fe oxide samples in comparison with the single metal oxide. Particularly, the peak positions of $2p_{3/2}$ level seem to be in close relations to the changing Ni/Fe ratio. After Fe is embedded in the NiO_x matrix, a notable chemical shift for both Ni and Fe $2p_{3/2}$ is found. With increasing proportion of Fe in bimetal oxides, the chemical shift for Ni $2p_{3/2}$ slightly increases, which accompanies a gradual decrease on chemical shift for Fe $2p_{3/2}$. However, the chemical shifts corresponding to Ni and Fe $2p_{3/2}$ levels are both diminished to almost zero, when the amount of Fe is up to 85.5 at.% (sample NF5). These results might indicate a strong interaction between nickel and iron atoms after addition of Fe. However, the interaction gradually reduces on the increment of Fe/Ni ratio, which might be owing to the deteriorated dispersion of Fe in NiO_x matrix and possible phase separation by aggregation individually at higher Fe/Ni ratios. In this regard, it can be proposed that at the optimal Fe/Ni ratio (3:7, sample NF3), the well distribution of iron species in NiO_x matrix exhibits a moderate interaction which might induce a better synergism to produce more surface active sites for OER. In previous work, some in situ spectroscopic studies, such as X-ray absorption, Mossbauer and Raman spectroscopy, have been carried out to find Ni(III), Fe(III), Fe(IV) or NiOOH species formed in crystalline Ni-Fe oxide catalyst at potentials relevant for electrochemical oxygen evolution [25,42–45]. In spite of these advances, the detailed mechanism is seemingly too complicated to be fully resolved at this point.

Apparent surface area is often an important factor to affect the catalytic activity. The relative ECSA of electrodes were determined by measuring the electrochemical capacitance of the film-electrolyte interface in the double-layer regime of the voltammograms [38]. The positive and negative capacitance currents at the center of the potential window were averaged and plotted against the scan rates. The obtained linear relationships for the as-investigated electrodes are plotted in Fig. 7, with partial amplification for sample NF1, NF2, NF4 and NF5 in the inset. Assuming that the intrinsic specific surface capacitance of all films is approximately the same, the relative surface area of the films can be determined. All electrodes demonstrate smaller ECSA, suggesting an intrinsic compact structure generally found for film materials prepared by sputtering technique [36,38–40]. Despite of this disadvantage, NF3 electrode shows the largest ECSA, which possibly means a large number of active sites distributed on its surface, leading to a better electrocatalytic performance. The ECSA decreases to nearly half for NiO_x electrode. While other bimetal oxide samples as well as FeO_x all demonstrate comparable ECSA, being much smaller than that of the NiO_x electrode. Thus, it can be seen that the Fe/Ni ratio is a crucial factor on the ECSA of as-prepared electrodes. The addition of Fe might block the surface active sites of NiO_x and result to a diminished ECSA in most cases. However, once at an optimal Fe/Ni ratio, more active sites might be generated due to a moderate interaction between NiO_x and FeO_x as proposed from above XPS analysis. Detailed mechanism is needed to be further investigated.

4. Conclusions

Using reactive magnetron co-sputtering technique, the optically transparent ($>50\%$) Ni-Fe oxide films with high electrochemical OER activities were successfully prepared at room temperature. At an atomic ratio of Fe/Ni = 3:7, the as-prepared bimetal oxide shows the optimal OER activity in aqueous KOH solution. The overpotentials at the current density of 2 and 5 mA cm^{-2} are 329 and 385 mV, respectively. This fabrication strategy is very promising to deposit optically transparent cocatalyst films over light harvesting photoelectrodes for improved PEC water splitting.

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References

- [1] A.J. Nozik, Photoelectrochemistry-applications to solar-energy conversion, *Annu. Rev. Phys. Chem.* 29 (1978) 189.
- [2] A.J. Bard, M.A. Fox, Artificial photosynthesis-solar splitting of water to hydrogen and oxygen, *Acc. Chem. Res.* 28 (1995) 141.
- [3] N.S. Lewis, D.G. Nocera, Powering the planet: Chemical challenges in solar energy utilization, *Proc. Natl. Acad. Sci. USA* 103 (2006) 15729.
- [4] A. Fujishima, K. Honda, Electrochemical photolysis of water at a semiconductor electrode, *Nature* 238 (1972) 37.
- [5] M.G. Walter, E.L. Warren, J.R. McKone, S.W. Boettcher, Q.X. Mi, E.A. Santori, N.S. Lewis, Solar water splitting cells, *Chem. Rev.* 110 (2010) 6446.
- [6] T.R. Cook, D.K. Dogutan, S.Y. Reece, Y. Surendranath, T.S. Teets, D.G. Nocera, Solar energy supply and storage for the legacy and nonlegacy worlds, *Chem. Rev.* 110 (2010) 6474.
- [7] X. Liu, F. Wang, Q. Wang, Nanostructure-based WO_3 photoanodes for photoelectrochemical water splitting, *Phys. Chem. Chem. Phys.* 14 (2012) 7894.
- [8] Z. Li, W. Luo, M. Zhang, J. Feng, Z. Zou, Photoelectrochemical cells for solar hydrogen production: current state of promising photoelectrodes, methods to improve their properties, and outlook, *Energy Environ. Sci.* 6 (2013) 347.
- [9] J.R. Swierk, T.E. Mallouk, Design and development of photoanodes for water-splitting dye-sensitized photoelectrochemical cells, *Chem. Soc. Rev.* 42 (2013) 2357.
- [10] Y. Park, K.J. McDonald, K.-S. Choi, Progress in bismuth vanadate photoanodes for use in solar water oxidation, *Chem. Soc. Rev.* 42 (2013) 2321.
- [11] T. Hisatomi, J. Kubota, K. Domen, Recent advances in semiconductors for photocatalytic and photoelectrochemical water splitting, *Chem. Soc. Rev.* 43 (2014) 7520.
- [12] B.A. Pinaud, J.D. Benck, L.C. Seitz, A.J. Forman, Z. Chen, T.G. Deutsch, B.D. James, K.N. Baum, G.N. Baum, S. Ardo, H. Wang, E. Miller, T.F. Jaramillo, Technical and economic feasibility of centralized facilities for solar hydrogen production via photocatalysis and photoelectrochemistry, *Energy Environ. Sci.* 6 (2013) 1983.
- [13] M.J. Kenney, M. Gong, Y. Li, J.Z. Wu, J. Feng, M. Lanza, H. Dai, High-performance silicon photoanodes passivated with ultrathin nickel films for water oxidation, *Science* 342 (2013) 836.
- [14] S. Hu, M.R. Shaner, J.A. Beardslee, M. Lichterman, Br. S. Brunenschwig, N.S. Lewis, Amorphous TiO_2 coatings stabilize Si GaAs, and GaP photoanodes for efficient water oxidation, *Science* 344 (2014) 1005.
- [15] C. Ding, J. Shi, D. Wang, Z. Wang, N. Wang, G. Liu, F. Xiong, C. Li, Visible light driven overall water splitting using cocatalyst/ BiVO_4 photoanode with minimized bias, *Phys. Chem. Chem. Phys.* 15 (2013) 4589.
- [16] C. Ding, W. Qin, N. Wang, G. Liu, Z. Wang, P. Yan, J. Shi, C. Li, Solar-to-hydrogen efficiency exceeding 2.5% achieved for overall water splitting with an all earth-abundant dual-photoelectrode, *Phys. Chem. Chem. Phys.* 16 (2014) 15608.
- [17] Y. Li, L. Zhang, A.T. -Pardo, J.M.G. -Calbet, Y. Ma, P. Oleynikov, O. Terasaki, S. Asahina, D. Shima, L. Zhao, K. Takanebe, J. Kubota, K. Domen, Cobalt phosphate-modified barium-doped tantalum nitride nanorod photoanode with 1.5% solar energy conversion efficiency, *Nat. Commun.* 4 (2013) 2566.
- [18] D.K. Zhong, M. Cornuz, K. Sivula, M. Gratzel, D.R. Gamelin, Photo-assisted electrodeposition of cobalt-phosphate (Co-Pi) catalyst on hematite photoanodes for solar water oxidation, *Energy Environ. Sci.* 4 (2011) 1759.
- [19] D.K. Zhong, D.R. Gamelin, Photoelectrochemical water oxidation by cobalt catalyst ("Co-Pi")/ $\text{r-Fe}_2\text{O}_3$ composite photoanodes: oxygen evolution and resolution of a kinetic bottleneck, *J. Am. Chem. Soc.* 132 (2010) 4202.
- [20] G. Liu, J. Shi, F. Zhang, Z. Chen, J. Han, C. Ding, S. Chen, Z. Wang, H. Han, C. Li, A tantalum nitride photoanode modified with a hole-storage layer for highly stable solar water splitting, *Angew. Chem. Int. Ed.* 53 (2014) 7295.
- [21] B. Klahr, S. Giménez, F. Fabregat-Santiago, J. Bisquert, T.W. Hamann, Photoelectrochemical and impedance spectroscopic investigation of water oxidation with "Co-Pi"-coated hematite electrodes, *J. Am. Chem. Soc.* 134 (2012) 16693.
- [22] E. Tsuji, A. Imanishi, K. Fukui, Y. Nakato, Electrocatalytic activity of amorphous RuO_2 electrode for oxygen evolution in an aqueous solution, *Electrochim. Acta* 56 (5) (2011) 2009.
- [23] T. Nakagawa, C.A. Beasley, R.W. Murray, Efficient electro-oxidation of water near its reversible potential by a mesoporous IrOx nanoparticle film, *Phys. Chem. C* 113 (2009) 12958.
- [24] Y. Matsumoto, E. Sato, Electrocatalytic properties of transition metal oxides for oxygen evolution reaction, *Mater. Chem. Phys.* 14 (1986) 397.
- [25] M.W. Louie, A.T.J. Bell, An investigation of thin-film Ni-Fe oxide catalysts for the electrochemical evolution of oxygen, *J. Am. Chem. Soc.* 135 (2013) 12329.
- [26] J. Landon, E. Demeter, N. Inoglu, C. Keturakis, I.E. Wachs, R. Vasic, A.I. Frenkel, J. R. Kitchin, Spectroscopic Characterization of Mixed Fe-Ni Oxide Electrocatalysts for the Oxygen Evolution Reaction in Alkaline Electrolytes, *ACS Catal.* 2 (2012) 1793.
- [27] M. Gong, Y.G. Li, H.L. Wang, Y.Y. Liang, J.Z. Wu, J.G. Zhou, J. Wang, T. Regier, F. Wei, H.J. Dai, An advanced Ni-Fe layered double hydroxide electrocatalyst for water oxidation, *J. Am. Chem. Soc.* 135 (23) (2013) 8452.
- [28] K.L. Hardee, A.J. Bard, Semiconductor electrodes V. The application of chemically vapor deposited iron oxide films to photosensitized electrolysis, *J. Electrochem. Soc.* 123 (1976) 1024.
- [29] A. Damjanovic, V. Brusio, Electrode kinetics of oxygen reduction on oxide-free platinum electrodes, *Electrochim. Acta* 12 (1967) 615.
- [30] D.A. Corrigan, The catalysis of the oxygen evolution reaction by iron impurities in thin film nickel oxide electrodes, *J. Electrochem. Soc.* 134 (1987) 377.
- [31] D. Grosso, F. Cagnol, G.J.D. Soler-Illia, E.L. Crepaldi, H. Amenitsch, A. Brunet-Bruneau, A. Bourgeois, C. Sanchez, Fundamentals of Mesostructuring Through Evaporation-Induced Self-Assembly, *Adv. Funct. Mater.* 14 (2004) 309.
- [32] Y.G. Wang, J.W. Ren, Y.Q. Wang, F.Y. Zhang, X.H. Liu, Y. Guo, G.Z. Lu, Nanocasted synthesis of mesoporous LaCoO_3 perovskite with extremely high surface area and excellent activity in methane combustion, *J. Phys. Chem. C* 112 (2008) 15293.
- [33] E. Guerrini, M. Piozzini, A. Castelli, A. Colombo, S.J. Trasatti, Effect of FeOx on the electrocatalytic properties of NiCo_2O_4 for O_2 evolution from alkaline solutions, *Solid State, Electrochem.* 12 (2008) 363.
- [34] S. Trasatti, G. Buzzanca, Ruthenium dioxide: a new interesting electrode material. Solid state structure and electrochemical behavior, *J. Electroanal. Chem.* 29 (1971) 1.
- [35] P. Castelli, S. Trasatti, F.H. Pollak, W.E. O'Grady, Single crystals as model electrocatalysts oxygen evolution on $\text{RuO}_2(110)$, *J. Electroanal. Chem.* 210 (1986) 189.
- [36] E.L. Miller, R.E. Rocheleau, Electrochemical behavior of reactively sputtered iron-doped nickel oxide, *J. Electrochem. Soc.* 144 (1997) 3072.
- [37] L. Kuai, J. Geng, C.Y. Chen, E.J. Kan, Y.D. Liu, Q. Wang, B.Y. Geng, A reliable aerosol-spray-assisted approach to produce and optimize amorphous metal oxide catalysts for electrochemical water splitting, *Angew. Chem. Int. Ed.* 53 (2014) 7547.
- [38] N. Wang, J. Zhu, X.J. Zheng, F.Q. Xiong, B.K. Huang, J.Y. Shi, C. Li, A facile two-step method for fabrication of plate-like WO_3 photoanode under mild conditions, *Faraday Discuss.* 176 (2014) 185.
- [39] H. Yan, R.N. Santoso, Y. Jiang, M.H. Liang, Z. Chen, Effect of oxygen concentration on the thermal stability of magnetron sputtered amorphous Ta-Ni thin films, *Thin Solid Films.* 520 (2012) 2356.
- [40] Y.X. Zhao, E.A. Hernandez-Pagan, N.M. Vargas-Barbosa, J.L. Dysart, T.E. Mallouk, A high yield synthesis of ligand-free iridium oxide nanoparticles with high electrocatalytic activity, *J. Phys. Chem. Lett.* 2 (2011) 402.
- [41] K. Sun, F.H. Saadi, M.F. Lichterman, W.G. Hale, H.-P. Wang, X. Zhou, N.T. Plymale, S.T. Omelchenko, J.-H. Hee, K.M. Papadantonakis, B.S. Brunenschwig, N. S. Lewis, Stable solar-driven oxidation of water by semiconducting photoanodes protected by transparent catalytic nickel oxide films, *Proc. Natl. Acad. Sci. USA* (2015), doi:http://dx.doi.org/10.1073/pnas.1423034112.
- [42] S.H. Kim, D.A. Tryk, M.R. Antonio, R. Carr, D.A. Scherson, In situ X-ray absorption fine structure studies of foreign metal ions in nickel hydrous oxide electrodes in alkaline electrolytes, *J. Phys. Chem.* 98 (1994) 10269.
- [43] M. Balasubramanian, C.A. Melendres, X-ray absorption spectroscopy studies of the local atomic and electronic structure of iron incorporated into electrodeposited hydrous nickel oxide films, *J. Phys. Chem. B* 104 (2000) 4300.
- [44] D.A. Corrigan, The catalysis of the oxygen evolution reaction by iron impurities in thin-film nickel-oxide electrodes, *J. Electrochem. Soc.* 134 (1987) 377.
- [45] L. Guerlou-Demourgues, L. Fournes, C. Delmas, In situ ^{57}Fe Mössbauer spectroscopy study of the electrochemical behavior of an iron-substituted nickel hydroxide electrode, *J. Electrochem. Soc.* 143 (1996) 3083.