Enhanced Oxygen Evolution Reaction Activity of Nanoporous SnO$_2$/Fe$_2$O$_3$/IrO$_2$ Thin Film Composite Electrodes with Ultralow Noble Metal Loading

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A conductive SnO$_2$ layer and small quantities of IrO$_2$ surface cocatalyst enhance the catalytic efficiency of nanoporous Fe$_2$O$_3$ electrodes in the oxygen evolution reaction at neutral pH. Anodic alumina templates are therefore coated with thin layers of SnO$_2$, Fe$_2$O$_3$, and IrO$_2$ by atomic layer deposition. In the first step, the Fe$_2$O$_3$ electrode is modified with a conductive SnO$_2$ layer and submitted to different postdeposition thermal treatments in order to maximize its catalytic performance. The combination of steady-state electrolysis, electrochemical impedance spectroscopy, X-ray crystallography, and X-ray photoelectron spectroscopy demonstrates that catalytic turnover and e$^-$ extraction are most efficient if both layers are amorphous in nature. In the second step, small quantities of IrO$_2$ with extremely low iridium loading of 7.5 µg cm$^{-2}$ are coated on the electrode surface. These electrodes reveal favorable long-term stability over at least 15 h and achieve maximized steady-state current densities of 0.57 ± 0.05 mA cm$^{-2}$ at $\eta$ = 0.38 V and pH 7 (1.36 ± 0.10 mA cm$^{-2}$ at $\eta$ = 0.48 V) in dark conditions. This architecture enables charge carrier separation and reduces the photoelectrochemical water oxidation onset by 300 mV with respect to pure Fe$_2$O$_3$ electrodes of identical geometry.

1. Introduction

To reach the global goal of an ample, sustainable, and carbon-free energy production, the efficient use of renewable energy sources is inalienable. Among renewable energy resources, the sun is the most striking candidate with its capability of satisfying the world's annual total energy consumption with less than an hour of solar energy.[1] However, solar energy utilization faces a major challenge in addition to the efficient capture and conversion of solar radiation itself, namely, the storage and transportation of the energy produced.[1,2] This latter aspect can be integrated into the former in the form of the photoelectrochemical (PEC) splitting of water into dioxygen and dihydrogen. This reaction offers the possibility to convert and store solar energy in form of chemical bonds directly.[3] Here, the oxidation of H$_2$O to O$_2$ has proven to be the more demanding half-reaction.[4] Among a great variety of suitable photoanode materials, iron oxide (Fe$_2$O$_3$) stands out as an abundant and inexpensive potential semiconductor and catalyst.[5] Fe$_2$O$_3$ also offers a favorable bandgap of 2.0–2.2 eV,[6] a valence band energy position sufficiently positive for the water oxidation reaction (2.4–2.7 V vs normal hydrogen electrode (NHE)),[7] and chemical stability in neutral and moderately basic pH.[6c,8] However, its slow oxygen evolution kinetics,[9] poor electrical conductivity (σ = 10$^{-12}$ Ω$^{-1}$ m$^{-1}$),[10] relatively large light absorption depth (α$^{-1}$ = 118 nm for a wavelength of λ = 550 nm),[11] short hole diffusion length (2–4 nm),[6c,12] and its correlated high rate of charge carrier recombination[9,11] limit the PEC anode efficiency.

Among the diverse approaches that have been applied to overcome these drawbacks, we will focus on the following three. 1) Efforts to nanostructure photoanodes and simultaneously reduce the iron oxide thickness have improved the water oxidation performance.[11b,14] Porosity in a macroscopically thick Fe$_2$O$_3$ layer enhances light collection while each individual structure may be microscopically thin in order to balance the development of an electrostatic field (depletion region) with a short charge carrier collection distance.[15] 2) Enhanced efficiencies can also be achieved by introducing a conductive scaffold
that collects and transports the photoexcited electrons and thereby avoids charge carrier recombination.\(^1\)\(^{15d,16} \) \(^2\) Fe\(_2\)O\(_3\) surfaces can be further modified with a particularly proficient water oxidation cocatalyst.\(^1\)\(^7\) The lower kinetic barrier of the cocatalyst facilitates an alternative pathway for the oxygen evolution reaction (OER). The fast consumption of holes by the chemical reaction minimizes their accumulation at the solid–liquid interface, and thereby their recombination with majority charge carriers.\(^1\)\(^7\)\(^a\)

Herein, we report a nanoporous SnO\(_2\)/Fe\(_2\)O\(_3\)/IrO\(_2\) thin film composite electrode with extremely low noble metal loading prepared by atomic layer deposition (ALD) for the OER under favorable benign (pH neutral) conditions. ALD is chosen as the deposition method due to its ability to conformally coat high aspect ratio substrates (anodic alumina) with precisely defined film thicknesses. The transparent SnO\(_2\) with its slightly lower conduction band energy\(^1\)\(^8\) and sufficient conductivity (at least 10\(^{11}\) times higher than d(Fe\(_2\)O\(_3\))\(^1\)\(^9\) fulfills the requirements for an electron collector. IrO\(_2\), as one of the most active OER catalyst materials, is ideal as the cocatalyst on the surface.\(^1\)\(^7\)\(^a\) We will proceed in two steps. At first, a conductive SnO\(_2\) layer is added to the nanoporous Fe\(_2\)O\(_3\) electrode and the system is characterized with respect to its morphology and phase composition. Since the crystallinity of the individual layers strongly influences their electronic properties, postdeposition thermal treatments are applied to the SnO\(_2\)/Fe\(_2\)O\(_3\) electrode. In the second step, the optimized SnO\(_2\)/Fe\(_2\)O\(_3\) electrode is additionally coated with small quantities of Ir\(_2\)O\(_3\) cocatalyst. These anodes reveal extremely low noble metal loadings of 7.5 \(\mu\)g cm\(^{-2}\) (standard OER loading: >1 mg cm\(^{-2}\))\(^1\)\(^{21}\)\(^b\) and favorable long-term stability under neutral conditions. In the dark, they achieve maximized steady-state current densities of 0.57 \(\pm\) 0.05 mA cm\(^{-2}\) at 0.38 V applied overpotential. Furthermore, the combination of the SnO\(_2\) conductive layer and IrO\(_2\) cocatalyst successfully separates photogenerated charge carriers, causing a shift of 300 mV to lower \(E\) with respect to pure Fe\(_2\)O\(_3\) electrodes.

2. Results and Discussion

2.1. Nanoporous SnO\(_2\)/Fe\(_2\)O\(_3\) Composite Electrodes

The type of nanoporous iron oxide electrodes optimized in earlier studies\(^2\)\(^2\) will first be modified with a conductive SnO\(_2\) layer. The preparation starts with an ordered array of parallel, cylindrical “anodic” Al\(_2\)O\(_3\) pores of \(\approx 370\) nm diameter (\(D\)) and 11 \(\mu\)m length (\(L\)) as the electrode template (see Figure S1, steps (a)–(e), in the Supporting Information). This template is functionalized with a micrometer-thick electrical Ni backside contact by sputter coating 100 nm of Au followed by galvanic deposition of Ni. The high aspect ratio substrate is subsequently coated with \(\approx 20\) nm of SnO\(_2\)\(^2\)\(^3\) followed by 10 nm of Fe\(_2\)O\(_3\)\(^2\)\(^{22b,23}\) via ALD. Scanning electron microscopy (SEM) images of an as-prepared electrode in top and cross-sectional views (Figure 1a,b) show the periodic arrangement of well-defined pores equipped with the Ni backside contact at the pore extremities (including \(\approx 1\) \(\mu\)m long Ni segments in the pores). The presence of Fe and Sn on the alumina template can be proven by energy-dispersive X-ray spectroscopy (EDX) element analysis (Figure 1c). EDX profiles recorded along the pores’ depth demonstrate that ALD is the suitable tool to coat the porous substrate with thin, continuous layers of SnO\(_2\) and Fe\(_2\)O\(_3\) (Figure 1d).

The chemical identity of the two individual layers is provided by X-ray photoelectron spectroscopy (XPS, Figure 2). The overview XPS spectrum of the nanoporous SnO\(_2\)-coated sample (Figure 2a) features only Sn, O, and C, whereas the Al\(_2\)O\(_3\) template is homogeneously covered and generates no Al signal. Deconvolution of the Sn 3d region (Figure 2b) reveals two peaks at 487.1 and 495.5 eV, which are consistent with Sn(IV) in SnO\(_2\).\(^2\)\(^{23,24}\) This assignment is confirmed by the deconvoluted O 1s peak centered at 531.0 eV (Figure 2c).\(^2\)\(^{23,24}\) Contributions at higher binding energies can be ascribed to adsorbed oxygen or the presence of water.\(^2\)\(^{23}\) After the deposition of the catalyst layer, conspicuous Fe peaks arise in the overview survey, whereas the Sn 3d signal almost vanishes (Figure 2a). This observation is reasonable since the iron oxide thickness is in the range of the average XPS analysis depth of 10 nm. The binding energies of 710.7, 724.2, and 529.8 eV for the Fe 2p\(_{3/2}\) and 2p\(_{1/2}\) and O 1s peaks, respectively, correspond to Fe(III) in Fe\(_2\)O\(_3\) (Figure 2c,d).\(^2\)\(^{22b,25}\) The nature of the conductive SnO\(_2\) layer remains unchanged with a marginal Sn 3d and O 1s peak shift to lower binding energies (Figure 2b,c). Furthermore, both layers are of amorphous nature since the X-ray diffraction (XRD) pattern (Figure 3) only features peaks of the crystalline Al template frame (Crystallographic Open Database, COD 9008460) and Au/Ni electrical contact (COD 1100138 and COD 2100649).

Since the crystallinity of the individual layers is often crucial for their functional performance,\(^1\)\(^{15d,22a,26}\) thermal treatments are applied to the SnO\(_2\) and Fe\(_2\)O\(_3\) layers with the objective of maximized catalytic turnover in the OER. Annealing (400 °C, N\(_2\)) of the conductive layer on its own provides...
crystalline cassiterite (SnO₂, COD 1000062), which subsequently results in a partially crystalline hematite (α-Fe₂O₃, COD 5910082) film growth upon ALD (Figure 3). In contrast to that, annealing both layers together (we will call this case “the SnO₂/Fe₂O₃ electrode annealed postdeposition”) results in pronounced crystalline cassiterite and hematite signals in the XRD pattern. The water oxidation performance of these differently treated electrodes is now studied by a combination of steady-state electrolysis (Figure 4) and electrochemical impedance spectroscopy (EIS, Figure 5) at \( E = +1.10 \text{ V vs Ag/AgCl (\( \eta = 0.48 \text{ V) in neutral pH conditions.} \) All three types of electrodes show two semicircles in the Nyquist plots (Figure 5a,b). The corresponding model (Figure 5c) therefore considers two interfaces, the liquid–solid and the solid–solid interface, each of them consisting of a charge-transfer resistance (\( R \)) and a non-ideal capacitor (\( Q \)). For the interpretation of the OER activity, both resistances \( R_{l/s} \) and \( R_{s/s} \) are of physical–chemical significance since they are directly related to the inherent catalytic activity and to the ability of electron (\( e^- \)) extraction (see Table S1 in the Supporting Information). The as-deposited amorphous SnO₂/Fe₂O₃ electrodes yield the lowest \( R_{s/s} \) and \( R_{l/s} \) values of 7 and 182 Ω cm⁻², as well as the highest current densities \( J = 171 \pm 17 \text{ µA cm}^{-2} \) (the uncertainty stated here refers to measurements performed on at least three nominally identical individual samples). The doubling of \( J \) relative to the pure nanoporous Fe₂O₃ electrode \cite{22c} proves the suitability of amorphous SnO₂ for efficient \( e^- \) extraction. Notably, any catalytic contributions of SnO₂ can be excluded by a control experiment (\( J = 0.3 \pm 0.3 \text{ µA cm}^{-2} \)). Thermal treatment of the conductive layer, however, reveals lower current densities and, additionally, an increase in \( R_{s/s} \) and \( R_{l/s} \) with respect to the as-deposited SnO₂/Fe₂O₃ electrode. This deterioration demonstrates that, first, the crystalline SnO₂ loses its function as a conductive layer and, second, the commencing crystallization of Fe₂O₃ reduces its catalytic activity. This trend is even more pronounced for

![Figure 2](image-url)  
*Figure 2. X-ray photoelectron spectra of the nanoporous SnO₂-coated template and the corresponding SnO₂/Fe₂O₃ composite electrode. All spectra are shifted to a C 1s binding energy of 284.8 eV. a) The survey spectra show the expected elements. Deconvolution of the core level spectra of b) Sn 3d, c) O 1s, and d) Fe 2p proves the SnO₂ and Fe₂O₃ chemical identities. The experimental data are provided as dashed lines, the fits as solid black lines, and the individual deconvoluted peaks are color coded.*

![Figure 3](image-url)  
*Figure 3. X-ray diffraction pattern of as-deposited and annealed SnO₂/Fe₂O₃ electrodes. A comparison is drawn between an as-deposited SnO₂/Fe₂O₃ electrode, an electrode with SnO₂ annealed on its own, (SnO₂)\(^T\)/Fe₂O₃, and an electrode annealed after the deposition of both layers, (SnO₂/Fe₂O₃)\(^T\). The signals corresponding to the Al frame (COD 9008460) and Au/Ni contact (COD 1100138, COD 2100649) are shown in black. The crystalline peaks of SnO₂ (COD 1000062) and α-Fe₂O₃ (COD 5910082) are highlighted in cyan and red, respectively.*

![Figure 4](image-url)  
*Figure 4. Steady-state current densities of nanoporous SnO₂/Fe₂O₃ electrodes for water oxidation at pH 7 (0.1 M KH₂PO₄ electrolyte) and +1.10 V vs Ag/AgCl (\( \eta = 0.48 \text{ V) in neutral pH conditions.} \) Comparison is drawn between the pure Fe₂O₃ electrode, the as-deposited SnO₂/Fe₂O₃ electrode (cyan bar), the composite electrode with annealed SnO₂ (blue bar), and the electrode annealed postdeposition (green bar). The error bars correspond to the values determined for at least three nominally identical individual samples.*
the electrodes annealed postdeposition with crystalline SnO$_2$ and Fe$_2$O$_3$. Here, $R_{ss}$ and $R_{ls}$ are $\approx 1.8$ and $\approx 5.2$ kΩ$^{-2}$, indicating a mismatch of the conduction band energy positions and a strongly reduced catalytic activity of crystalline Fe$_2$O$_3$. The lower water oxidation efficiency of crystalline Fe$_2$O$_3$ is in line with earlier studies on nanoporous Fe$_2$O$_3$ electrodes. [22c] In summary, the amorphous nature of the as-deposited nanoporous SnO$_2$/Fe$_2$O$_3$ composite electrode proves to be ideal for a maximized OER activity. This electrode architecture represents the basis for subsequent electrode modification.

### 2.2. Nanoporous SnO$_2$/Fe$_2$O$_3$/IrO$_2$ Composite Electrodes

In the second part, an IrO$_2$ cocatalyst is applied to the optimized nanoporous SnO$_2$/Fe$_2$O$_3$ electrode. However, the introduction of the low-abundance and expensive IrO$_2$ requires the minimization of its loading. Therefore, only seven ALD cycles of iridium oxide (significantly less than 1 nm) are deposited on top of the nanoporous SnO$_2$/Fe$_2$O$_3$ electrode (step (f) in Figure S1, Supporting Information). The successful deposition is demonstrated by EDX (Figure S2, Supporting Information) and XPS (Figure 6). This very low IrO$_2$ loading is, however, not observable in transmission electron microscopy (TEM, Figure S3, Supporting Information). The analysis of the XPS survey (Figure 6a) shows the presence of Ir, O, Fe, and C, whereas Sn is not detectable any longer. The Fe 2p peaks and thus the iron oxide chemical identity remain unchanged upon cocatalyst coating (Figure 6b,c). Deconvolution of the Ir 4f region reveals two doublets for two chemically distinct Ir environments (Figure 6d). Their Ir 4f$_{7/2}$ maxima centered at 61.9 and 62.7 eV are consistent with IrO$_2$ and hydrated Ir(IV) oxide, respectively.[28] This observation is also confirmed by the O 1s region (Figure 6c). Furthermore, the seven cycles of IrO$_2$ coating correspond to an ultralow iridium loading of 7.5 µg cm$^{-2}$ as quantified by inductively coupled plasma optical emission spectrometry (ICP-OES).

To quantify the effectiveness of the nanoporous SnO$_2$/Fe$_2$O$_3$/IrO$_2$ electrodes in the OER, the steady-state current densities are compared to those of pure Fe$_2$O$_3$, SnO$_2$/Fe$_2$O$_3$, and Fe$_2$O$_3$/IrO$_2$ electrodes (Figure 7). At an applied overpotential of $\eta = 0.48$ V, SnO$_2$/Fe$_2$O$_3$/IrO$_2$ electrodes achieve $1.36 \pm 0.10$ mA cm$^{-2}$ (Figure 7a). This value corresponds to a $J$ improvement by factors of 8 and 17 with respect to SnO$_2$/Fe$_2$O$_3$ and pure Fe$_2$O$_3$ electrodes, respectively. In contrast to that, the application of an IrO$_2$ coating on the as-deposited Fe$_2$O$_3$ electrode only yields $0.11 \pm 0.02$ mA cm$^{-2}$ even with ten ALD cycles. Control experiments with SnO$_2$/IrO$_2$ electrodes ($J = 0.01 \pm 0.01$ mA cm$^{-2}$) additionally prove the need for the three-layer architecture. Any contributions of the nickel electrical contact to the overall $J$ are small ($J = 0.03$ mA cm$^{-2}$ from our control experiments) and therefore negligible. The effect of ozone treatment on the Fe$_2$O$_3$ surface upon IrO$_2$ deposition cannot be the cause for the
performance improvement, since Fe₂O₃ is also deposited with O₃ at almost the same temperature. Even more convincing is the SnO₂/Fe₂O₃/IrO₂ electrode performance at lower η shown in the corresponding Tafel plot (Figure 7b). Reducing η to 0.38 V still yields 0.57 ± 0.05 mA cm⁻²—a 188-fold improvement relative to pure Fe₂O₃. At η = 0.28 V, they enable an OER turnover that exceeds those of Fe₂O₃ electrodes even by a factor of 1925, or, equivalently, 3.3 decimal logarithmic units. These electrodes additionally reveal favorable long-term stability over at least 15 h of steady-state electrolysis (Figure S4, Supporting Information) without measurable loss of the IrO₂ cocatalyst (Figure S2, Supporting Information). The nanoporous Fe₂O₃, Fe₂O₃/IrO₂, and SnO₂/Fe₂O₃/IrO₂ electrodes are characterized by nonlinear Tafel plots, with slopes increasing from 60 ± 10 mV per decade at low applied overpotential (η ≤ 0.48 V) to 170 ± 15 mV per decade at η ≥ 0.48 V. In comparison, the SnO₂/Fe₂O₃/IrO₂ electrodes yield η = 150 and = 580 mV per decade in these two regimes, respectively. Such large values of the Tafel slopes are characteristic of an OER that is no longer limited by the catalytic turnover at the surface, but by mass/charge transport in the pores.[27] In practical terms, they express that our nanoporous electrodes are most efficient at lower applied overpotentials.

Based on these results and the band alignment of our semiconductors (Figure 8),[7a,29] we expect a photoelectrochemical activity upon solar irradiation. The experimental data are presented in Figure 9 and Figure S5 in the Supporting Information. The initial system, the nanoporous Fe₂O₃ electrode, only yields negligible photocurrents (Figure 9a). The lack of photoresponse probably results from both the slow water oxidation kinetics and the low semiconductor conductivity, a combination associated with predominant charge carrier recombination.[10,15b,d] Lowering the OER kinetic barrier with the IrO₂ cocatalyst reveals no significant difference with respect to the Fe₂O₃ electrode (Figure 9b). Thus, e⁻ transport in the semiconductor layer must be the major limiting factor. Indeed, with SnO₂ as a conductive layer (but no IrO₂), a clear shift of ~170 mV (at J = 0.2 mA cm⁻²) can be observed upon illumination in the J–E curve (Figure 9c). This shift demonstrates that photoinduced e⁻ are efficiently extracted via the conductive SnO₂ layer. Consequently, the SnO₂/Fe₂O₃ photoanode performance is now limited by the OER kinetics. By adding both functional materials to one Fe₂O₃ electrode, the best PEC performance can be achieved with a shift of 300 mV to lower E (at J = 0.2 mA cm⁻²) relative to the pure Fe₂O₃ electrode (Figure 9d). In this system, e⁻ extraction and H₂O oxidation turnover are in fact so efficient that transport of ions in the pores becomes the limiting factor at a certain applied potential (observable as a peak at +1.1 V). A rough approximation of the external photoelectrochemical quantum efficiency reached in these conditions can be obtained by comparing our current density (on the order of 0.44 mA cm⁻²) at 0.38 V overpotential for SnO₂/Fe₂O₃ with the solar photon flux between 2.1 eV (bandgap of Fe₂O₃)[6] and 3.8 eV (bandgap of SnO₂)[24] yielding 4%.[30] This value is lower than efficiencies reported for similar Fe₂O₃-based electrodes (Table S2, Figure 9).
Supporting Information). However, all of them are applied in strongly alkaline medium (pH 13.6), which is associated with a larger driving force from the Fe\textsubscript{2}O\textsubscript{3} valence band edge (by \(\approx 0.4\) V) and thus influences charge separation favorably.

3. Conclusions

Nanoporous SnO\textsubscript{2}/Fe\textsubscript{2}O\textsubscript{3}/IrO\textsubscript{2} thin film composite electrodes, suitable for the OER in neutral media, have been successfully prepared by atomic layer deposition. If the nanoporous Fe\textsubscript{2}O\textsubscript{3} is first modified with a conductive SnO\textsubscript{2} layer only, efficient e\textsuperscript{-} extraction and maximized catalytic turnover are only achieved if both SnO\textsubscript{2} and Fe\textsubscript{2}O\textsubscript{3} are amorphous. In contrast to that, thermal annealing crystallizes SnO\textsubscript{2} and Fe\textsubscript{2}O\textsubscript{3} and thereby deteriorates both desired properties. Taking this knowledge as a basis, the as-deposited SnO\textsubscript{2}/Fe\textsubscript{2}O\textsubscript{3} electrodes are subsequently further modified with seven ALD cycles of IrO\textsubscript{2}. These composite electrodes reveal extremely low noble metal loadings of 7.5 \(\mu\)g cm\textsuperscript{-2} and desirable long-term stability for at least 15 h of steady-state electrolysis. In the dark, our nanoporous SnO\textsubscript{2}/Fe\textsubscript{2}O\textsubscript{3}/IrO\textsubscript{2} electrode yields maximized steady-state current densities of 0.57 \(\pm\) 0.05 mA cm\textsuperscript{-2} at \(\eta = 0.38\) V corresponding to a 188-fold improvement with respect to pure Fe\textsubscript{2}O\textsubscript{3} electrodes. The reduction of \(\eta\) to 0.28 V even enhances the J improvement factor to a value of 1925. We want to highlight here that this performance is achieved under favorable benign (pH neutral) conditions, whereas most other Fe\textsubscript{2}O\textsubscript{3} electrodes of similar architecture are applied in strongly basic conditions.[15d,16d,17a,b,29a,31] Using an alkaline medium also improves the performance of our Fe\textsubscript{2}O\textsubscript{3}-based electrodes significantly, as expected (see Figure S6 in the Supporting Information), however, at the expense of a lack of long-term stability.[17d] In fact, our stable dark currents measured at \(\eta = 0.38\) V in neutral media outperform those of most Fe\textsubscript{2}O\textsubscript{3}-based electrodes (some featuring a transparent conductive oxide scaffold and/or an IrO\textsubscript{2} cocatalyst coating) independent of their pH conditions (Table S3, Supporting Information).[16d,17a,29a,31]

Additionally, the improved catalytic turnover combined with efficient charge carrier separation allows for a significant shift in the photocurrent response by 300 mV to lower \(E\) with respect to pure Fe\textsubscript{2}O\textsubscript{3} electrodes.

4. Experimental Section

**Materials:** Chemicals were purchased from Sigma-Aldrich, Alfa Aesar, ABCR, Strem, or VWR and used as received. Water was purified in a Millipore Direct-Q system for application in electrolytes. Aluminum plates (99.999%) and Si(100) wafers covered with an oxide layer were purchased from ABCR, Strem, or VWR and used as received. Water was purified in a Millipore Direct-Q system for application in electrolytes. Aluminum plates (99.99%) and Si(100) wafers covered with an oxide layer were purchased from ABCR, Strem, or VWR and used as received.

**Preparation of Nanostructured Composite Electrodes:** Nanstructured composite electrodes were prepared in a multistep procedure as illustrated in Figure S1 in the Supporting Information. First the nanoporous alumina oxide templates were obtained via the standard two-step anodization of aluminum (represented as (a) in Figure S1 in the Supporting Information).[13] Homemade two-electrode cells consisting of a polyvinyl chloride beaker with four circular openings at the bottom were used to anodize aluminum plates of 2.2 cm diameter, which were therefore held between an O-ring and a thick copper plate operating as an electrical contact. Adequate cooling of the beaker was ensured via a cold plate connected to a closed-circuit cooler by Haake.

Each beaker was filled with electrolyte and closed with a lid containing a mechanical stirrer and silver wire mesh as the counter electrode. The whole setup was thermally insulated laterally. The aluminum plates were electropolished in a cooled perchloric acid/ethanol solution (1:3 v/v HClO\textsubscript{4}/EtOH) for 5 min under +200 V, rinsed, and cooled before anodizing them under +195 V for 23 h at 0 °C in 1 wt% H\textsubscript{2}PO\textsubscript{4}. The disordered, porous Al\textsubscript{2}O\textsubscript{3} generated was then removed in a chromic acid solution (0.18 m H\textsubscript{2}O\textsubscript{2} in 6 wt% H\textsubscript{2}PO\textsubscript{4}) for 23 h at 45 °C. The second anodization was subsequently performed for 4 h at 0 °C in 1 wt% H\textsubscript{2}PO\textsubscript{4} yielding the well-ordered Al\textsubscript{2}O\textsubscript{3} matrix. The next step involved the removal of the metallic Al on the backside of the anodized Al\textsubscript{2}O\textsubscript{3} with 0.7 m CuCl\textsubscript{2} solution in 10% HCl, followed by opening the Al\textsubscript{2}O\textsubscript{3} barrier layer closing the pores with simultaneous isotropic pore widening in 10 wt% H\textsubscript{2}PO\textsubscript{4} for 39 min (step (b) in Figure S1, Supporting Information). The AAO template was subsequently equipped with an electrical contact at one side of pore extremities (step (c) in Figure S1, Supporting Information). To this goal, 100 nm of gold was deposited on the templates in a Torr CRC 622 sputter coater operating in DC mode for subsequent electrodeposition of a thicker nickel contact. Ni was electropolated from a diluted Watts electrolyte (0.57 m NiSO\textsubscript{4}+6H\textsubscript{2}O, 95 \(\times\) 10\textsuperscript{-3} m NiCl\textsubscript{2}+6H\textsubscript{2}O, and 0.5 m H\textsubscript{2}BO\textsubscript{3} adjusted to pH 3.0) in a two-electrode configuration with a Pt mesh as counter electrode under −2.3 V for 4 h. The final AAO templates were then coated by atomic layer deposition. The deposition of SnO\textsubscript{2} was performed in a commercial Gemstar-6 XT ALD reactor from Arradiance operating with N\textsubscript{2} as carrier gas (step (d) in Figure S1, Supporting Information). ALD was carried out at 200 °C with tetakis(dimethylamino)tin(IV) and H\textsubscript{2}O\textsubscript{2} both kept in stainless steel bottles maintained at 60 °C and room temperature, respectively. The pulse, exposure, and purge times for both precursors were 0.5, 40, and 120 s, respectively. 430 ALD cycles yielded \(\approx 20\) nm of SnO\textsubscript{2}.[23] Fe\textsubscript{2}O\textsubscript{3} was deposited in a home-built hot-wall reactor fitted with a chemically resistant diaphragm pump MV10C from Vacuubrand (step (e) in Figure S1, Supporting Information). The ALD process was performed with N\textsubscript{2} as carrier gas at a chamber temperature of 200 °C. Ferrocene (C\textsubscript{6}P\textsubscript{6}Fe, kept in a stainless steel bottle maintained at 70 °C) and ozone were used as precursors with pulse, exposure, and purge times of 2, 40, and 60, 0.2, 40, and 60 s, respectively. 800 ALD cycles were performed in order to obtain \(\approx 10\) nm of Fe\textsubscript{2}O\textsubscript{3} on the functional samples.[22b] The IrO\textsubscript{2} deposition was carried out with ethylicyclopentadienyl-1,3-cyclohexadieneiridium(I) ((EtCp)\textsubscript{3}Ir(CHD), kept at 90 °C in a stainless steel bottle) and O\textsubscript{3} at 220 °C in the commercial Gemstar-6 XT ALD reactor (step (f) in Figure S1, Supporting Information). Four consecutive microcycles each consisting of a 0.5 s (EtCp)\textsubscript{3}Ir(CHD) pulse and 40 s of exposure time were performed before the chamber was purged with N\textsubscript{2} for 90 s. Ozone was introduced in a single pulse of 0.5 s, whereas exposure and purge durations were 40 and 90 s, respectively. Seven or ten macrocycles were used for the cocatalyst coatings. Approximately 10 nm of IrO\textsubscript{2} was deposited with 150 macrocycles for control experiments.[27] For the determination of the Fe\textsubscript{2}O\textsubscript{3}, SnO\textsubscript{2}, and IrO\textsubscript{2} layer thicknesses, silicon wafers coated with Al\textsubscript{2}O\textsubscript{3} or indium-doped tin oxide were added to the reaction chamber and subsequently characterized by spectroscopic ellipsometry.

**Annealings:** Samples having undergone the complete preparative procedure were annealed in a muffle furnace from Nabertherm under N\textsubscript{2} atmosphere. The nanoporous samples were heated up to 400 °C over 12 h, maintained at this temperature for 4 h, and cooled down to room temperature over 12 h.

**Instrumental Methods:** The Fe\textsubscript{2}O\textsubscript{3} and SnO\textsubscript{2} layer thicknesses were determined on Si(100) wafers with a Sentech spectroscopic ellipsometer SENpro equipped with a tungsten halogen lamp. 50 data points were recorded for wavelengths between 380 and 1050 nm under an angle of 70° for each measurement. The software SpectraRay/3 was used to fit the data orientation (Θ) and ellipiticity (ε) with fixed optical models for Fe\textsubscript{2}O\textsubscript{3} and SnO\textsubscript{2}. SEM and EDX were carried out on a JEOL JSM 6400 PC implemented with a LaB\textsubscript{6} cathode and SDD X-ray detector. Further SEM images and EDX spectra were recorded with a Zeiss EVO 40 microscope.
Supporting Information

Supporting Information is available from the Wiley Online Library or Supporting Information

Conflict of Interest

The authors declare no conflict of interest.

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