Preparative History vs Driving Force in Water Oxidation Catalysis: Parameter Space Studies of Cobalt Spinels

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ABSTRACT: The development of efficient, stable, and economic water oxidation catalysts (WOCs) is a forefront topic of sustainable energy research. We newly present a comprehensive three-step approach to systematically investigate challenging relationships among preparative history, properties, and performance in heterogeneous WOCs. To this end, we studied (1) the influence of the preparative method on the material properties and (2) their correlation with the performance as (3) a function of the catalytic test method. Spinel-type Co₃O₄ was selected as a clear-cut model WOC and synthesized via nine different preparative routes. In search of the key material properties for high catalytic performance, these cobalt oxide samples were characterized with a wide range of analytical methods, including X-ray absorption spectroscopy, X-ray photoelectron spectroscopy, powder X-ray diffraction, Raman spectroscopy, BET surface area analysis, and transmission electron microscopy. Next, the corresponding catalytic water oxidation activities were assessed with the three most widely applied protocols to date, namely, photocatalytic, electrocatalytic, and chemical oxidation. The activity of the Co₃O₄ samples was found to clearly depend on the applied test method. Increasing surface area and disorder as well as a decrease in oxidation states arising from low synthesis temperatures were identified as key parameters for high chemical oxidation activity. Surprisingly, no obvious property–performance correlations were found for photocatalytic water oxidation. In sharp contrast, all samples showed similar activity in electrochemical water oxidation. The substantial performance differences between the applied protocols demonstrate that control and comprehensive understanding of the preparative history are crucial for establishing reliable structure–performance relationships in WOC design.

INTRODUCTION

Efficient water splitting, also referred to as artificial photosynthesis, provides direct access to storable and renewable fuels.¹⁻⁵ The complex four-electron transfer of the water oxidation half reaction remains a major bottleneck for designing high-performance water splitting systems.⁶ Therefore, the development of stable, economic, and efficient water oxidation catalysts (WOCs) is essential for water splitting technologies.⁷,⁸

However, the quest for optimal WOCs remains largely empirical due to fundamental open questions in solid-state synthesis. First, the predictivity of inorganic synthetic protocols is still limited, especially with respect to understanding the precise influence of diverse synthetic methods and conditions on crucial material parameters.⁹⁻¹³ Consequently, establishing predictive preparation–properties–performance relations for WOCs remains a fundamental challenge. Moreover, recent results indicate that the key parameters required for optimal WOC performance can vary significantly with the applied catalytic test method.¹⁴⁻¹⁶ Few systematic studies to date shed light on the understanding of preparative history as an essential foundation for catalyst production, which is indispensable for true material tailoring and any large-scale production processes. In the long term, screening such wide parameter spaces may only be possible with new, tailored machine learning approaches.¹⁷,¹⁸

We here introduce a new, comprehensive strategy to investigate the complex interplay of preparation, emerging properties, and assay-dependent performance for Co₃O₄ as a straightforward, binary WOC model system.

In the ongoing search for abundant, low-cost, and robust alternatives to noble metals,¹⁶,¹⁷ spinel-type Co₃O₄ keeps attracting attention.¹⁹⁻⁻²¹ Furthermore, Co₃O₄ is investigated for a wide range of other applications, for example, in battery electrodes,²²⁻²⁵ sensors,²⁶ data storage,²⁶ as well as in general heterogeneous catalysis.²⁷,²⁸ Therefore, considerable attempts have been made to improve the oxygen evolution reaction (OER) performance of pristine Co₃O₄, which is limited by...
conductivity and the number of exposed surface active sites.\textsuperscript{29} To this end, various specific properties were addressed, such as crystallinity,\textsuperscript{30,31} oxidation states,\textsuperscript{32,33} particle/crystallite size,\textsuperscript{34,35} defects,\textsuperscript{36} crystal structure,\textsuperscript{37−40} surface area,\textsuperscript{41} and morphology.\textsuperscript{32,43,29} Defects in particular can exert a great influence on the interaction between the reactants and the catalyst surface.\textsuperscript{44−48} While oxygen defects in Co\textsubscript{3}O\textsubscript{4} created a higher amount of active Co(II) surface species, cobalt deficiencies were found to enhance the surface wettability.\textsuperscript{44,45} Furthermore, the productive influence of edge dislocation defects on the electrochemical performance of Co\textsubscript{3}O\textsubscript{4} was newly explored.\textsuperscript{49} Additionally, a wide range of different synthetic methods was applied on Co\textsubscript{3}O\textsubscript{4} in the course of individual studies, including molten salt (MS),\textsuperscript{50} ball milling (BM),\textsuperscript{51} sol−gel (SG),\textsuperscript{52} thermal decomposition (TD),\textsuperscript{53,54} precipitation,\textsuperscript{55} and classic/microwave hydrothermal (MW) synthesis.\textsuperscript{56,57,21} Generally, deriving clear preparation−performance trends from comparisons between different studies remains difficult due to the underlying variations in the obtained material properties.\textsuperscript{58−60} To the best of our knowledge, the impact of the manifold preparative options on the catalytic efficiency of Co\textsubscript{3}O\textsubscript{4} in different test methods has not been evaluated coherently to date. The three most common routine tests are (1) photochemical oxidation with the well-established [Ru(bpy)]\textsubscript{3}\textsuperscript{2+/S\textsubscript{2}O\textsubscript{8}\textsuperscript{2−}/visible-light assay, (2) chemical oxidation, typically performed with ceric ammonium nitrate (CAN), and (3) electrochemical methods.\textsuperscript{15,61−63} More emphasis in electrochemical catalysis was hitherto placed on identifying the true active species for Co-oxide-assisted water oxidation.\textsuperscript{64−67} Recently, two in situ studies revealed that the observed process was in fact reversible and associated with the formation of a cobalt oxyhydroxide layer during electrocatalysis.\textsuperscript{31,32,67} Notwithstanding, critical comparisons between two or more catalytic test assays for a given WOC remain quite rare, so that activity trends for one assessment method were often assumed to be valid for another. Only in 2015, a pioneering study by Stahl et al.\textsuperscript{14} first critically evaluated the influence of the employed oxidation method on the activity of different manganese oxide WOCs and demonstrated that the “best catalyst” indeed depends on the applied oxidation method. Furthermore, Ding et al.\textsuperscript{68,69} found a related dependence on the applied protocol for iron-based oxides doped with different elements and iron-based polyoxometalates. These results on select systems demonstrate the general necessity for further studies into the complex parameter space of catalyst preparation, properties, and test protocols.

We here pave new ways to assess WOCs unambiguously with a systematic three-step methodology that stands out through screening a wide synthetic parameter space for emerging properties−performance relations. Co\textsubscript{3}O\textsubscript{4} as a

Figure 1. TEM images of representative Co\textsubscript{3}O\textsubscript{4} samples prepared by different synthesis methods: (a) MW-A, (b) MW-B, (c) HT-A, (d) HT-B, (e) PM, (f) SG, (g) MS, (h) BM, and (i) TD (scale bar = 80 nm).
model WOC was (1) accessed with a wide spectrum of synthetic methods. (2) The influence of these preparative routes on the WOC activity was specifically assessed with the three most established catalytic test methods. (3) The emerging properties–performance trends were then substantiated with thorough syncharacterizations of the different Co₃O₄ materials with a wide analytical repertoire, including surface analyses, diffraction, spectroscopy, and microscopy techniques. This strategy brought forward new correlations between the preparative history of Co₃O₄ specimens with both their resulting material properties and the catalytic performance in different water oxidation setups.

**RESULTS AND DISCUSSION**

**Characterization of the Different Co₃O₄ Materials.** The synthesized cobalt oxides were labeled according to the applied synthesis method: microwave hydrothermal (MW), hydrothermal (HT), precipitation method (PM), sol–gel (SG), molten salt (MS), ball milling (BM), and thermal decomposition (TD). Further information on the specific synthetic protocols is provided in the Experimental Section and Methods.

**Transmission Electron Microscopy (TEM) and Brunauer–Emmett–Teller (BET) Surface Area Characterizations.** Representative TEM images of Co₃O₄ samples emerging from the nine different synthetic protocols are shown in Figure 1. The synthetic methods exerted a clear influence on the resulting morphologies. The spinel cobalt oxides prepared by (microwave) hydrothermal synthesis (Figure 1a,b,d) and by the precipitation method (Figure 1e) show agglomerated nanoparticles in a size range 5–15 and 25 nm, respectively. The Co₃O₄ samples synthesized by a different hydrothermal procedure or by ball milling and thermal decomposition (Figure 1c,h,i) partially consist of elongated nanoparticles with an average size distribution around 50 nm. The particles shown in Figure 1f,g were prepared by sol–gel and molten salt methods, respectively, and they exhibit significantly larger particle sizes of more than 300 nm.

Furthermore, the surface area values of all samples were determined from their measured N₂-sorption isotherms with the Brunauer–Emmett–Teller (BET) model. The values are given in Table 1 and are in line with the TEM images, as well as with the general trend of smaller particles showing a higher surface area and vice versa.

**Powder X-ray Diffraction (PXRD).** The powder X-ray diffraction (PXRD) data in Figure 2a show the patterns for all synthesized Co₃O₄ samples that display the spinel-type structure throughout (space group Fd̅3m (No.: 227)). In the normal spinel structure, the O²⁻ anions form a cubic close-packed lattice, where octahedral and tetrahedral sites are occupied by the Co³⁺ and Co²⁺ cations, respectively. Although all Bragg reflections are in agreement with the given reference (PDF Card No.: 01-080-1544), the full width at half-maximum (FWHM) is different for all synthesized cobalt oxides. As the crystallite domain size τₓₓᵧᵧ (Figure 2b and Table 1) was used to calculate τₓₓᵧᵧ as shown in Figure 2c and Table 1. As expected, the cobalt oxides synthesized at higher temperatures (≥2400 °C), namely, SG, MS, BM, and TD, display a high crystalline domain size from ≈91 nm (SG) and up to ≈141 nm (MS). The cobalt oxide samples obtained at lower temperatures (≤180 °C), that is, MW-A, MW-B, HT-B, and PM, show a much lower crystallite domain size with values below ≈25 nm (PM) and down to ≈7 nm (MW-A). HT-A is the only exception to this trend with a higher τₓₓᵧᵧ of ≈96 nm.

**Raman Spectroscopy and PXRD Characterization.** The Raman spectra of all synthesized cobalt oxides are shown in Figure 2c. The group theory predicts five Raman-active vibrations for the normal spinel structure
vibrational modes for \( \text{Co}_3\text{O}_4 \) consisting of \( \text{A}_{1g} \text{E}_{g} \) and three \( \text{F}_{2g} \) modes.\(^{72}\) These five main phonon excitations were observed for all spectra and match well with theoretical and experimental reports on spinel-type cobalt oxide.\(^{73,74}\) The symmetric \( \text{Co}^{3+} \text{O} \) stretching vibration of octahedrally coordinated \( \text{Co}_3\text{O}_4 \) is attributed to \( \text{A}_{1g} \) in \( \text{O}_{6} \) symmetry and is assigned to the most intense band at \( \approx 690 \text{ cm}^{-1} \). The medium-/low-intensity bands at \( \approx 620, \approx 520, \text{ and } \approx 480 \text{ cm}^{-1} \) correspond to \( \text{E}_{2g} \text{F}_{2g} \text{ and } \text{E}_{g} \) symmetry. The band at \( \approx 190 \text{ cm}^{-1} \) arises from tetrahedrally coordinated \( \text{Co}^{2+} \text{O}_4 \) units with \( \text{F}_{2g} \text{ symmetry. These results further confirm the formation of phase-pure cubic spinel } \text{Co}_3\text{O}_4 \text{ from all applied synthesis methods.}

Generally, narrow and intense Raman-active modes are indicative of well-ordered structures. In the present system, the oxides emerging from low-temperature methods (MW-A, MW-B, HT-B, HT-A) exhibit Raman peaks shifted toward higher-frequency values. They display lower intensity and peak broadening (Table S1) when compared with the oxide samples obtained at higher temperatures (SG, MS, BM, TD). This trend indicates a decrease in the long-range order of oxides synthesized at low temperatures (MW-A, MW-B, HT-B, PM). Likewise, their PXRD patterns display low intensities and peak broadening (MW-A, MW-B, HT-B, P, Figure 2a).\(^{75}\) Among them, the pattern of \( \text{Co}_3\text{O}_4\text{-HT-B} \text{ shows tremendous peak broadening. This can be explained by the smaller particle size and increased disorder as described below.}

The observed variations in the Raman symmetry and PXRD patterns further suggest that the tetrahedral and octahedral coordination environments in the different \( \text{Co}_3\text{O}_4 \) specimens depend on the applied synthetic methods. The irregular cation bond strength\(^{76}\) induces lattice distortions and residual stress in the spinel structure, which could result from the formation of oxygen or cobalt vacancies and weaken the average Co–O bond strength.\(^{76}\)

**X-ray Absorption Spectroscopy (XAS).** To acquire deeper insights into the atomic short-range order of the as-synthesized cobalt oxides, X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) analyses were carried out. Figure 3 shows the fitting of the Fourier-transform (FT)\( k^{3}\chi(k) \) spectra of the experimental Co K edge EXAFS spectra \( k^{3}\chi(k) \), for oxides displaying remarkable differences in their short-range order, that is, \( \text{Co}_3\text{O}_4\text{-SG, -MS, -PM, -MW-A, -MW-B, and -HT-B} \). The \( \text{Co}_3\text{O}_4\text{-BM, -TD, and -HT-A} \) oxides show a short-range order similar to that of \( \text{Co}_3\text{O}_4\text{-PM} \), and the fitting results of their FT\( k^{3}\chi(k) \) spectra are presented in Figure S2. Calculated main values for interatomic distances, atomic coordination numbers (N), and Debye-Waller factors (\( \sigma^2 \)) are given in Table S2.

All synthesized \( \text{Co}_3\text{O}_4 \) samples show four prominent peaks arising from backscattering of neighboring O and Co atoms. The first peak in the FT\( k^{3}\chi(k) \) spectra at \( r \approx 1.55 \text{ Å} \) relates to \( \text{Co}^{3+} \) and \( \text{Co}^{3+} \) cations in tetrahedral \{\( \text{Co}_4 \)\} and octahedral \{\( \text{Co}_3 \)\} coordination with oxygen atoms at interatomic distances of \( \approx 1.914 \text{ } \text{ Å} \). However, since those two shells are too close to be resolved in the FT\( k^{3}\chi(k) \) spectra, they convolute to a first Co–O shell with a main interatomic distance Co–O \( \approx 1.907 \text{ Å} \) and an averaged atomic coordination number \( n = 5.333 \). The second and third peaks in the FT\( k^{3}\chi(k) \) spectra, at \( r \approx 2.49 \text{ and } 2.95 \text{ Å} \), correspond to the \( \text{Co}_{\text{octa}} \text{-Co}_{\text{octa}} \approx 2.86 \text{ Å} \) [\( n = 4 \) and \( \text{Co}_{\text{tetra}} \text{-Co}_{\text{octa}} \approx 3.35 \text{ Å} \) [\( n = 8 \)]] coordination shells. The fourth peak at \( r \approx 4.70 \text{ Å} \) relates to higher Co and O coordination shells (Figure 3 and Table S2). Remarkably, while the relative amplitude of the first Co–O coordination shell in the FT\( k^{3}\chi(k) \) and wavelet-transform (WT) spectra \( r \approx 1.55 \text{ Å} \) does not change much among the different \( \text{Co}_3\text{O}_4 \) oxides, the FT\( k^{3}\chi(k) \) and WT spectra show a decreasing relative magnitude of the \( \text{Co}_{\text{octa}} \text{-Co}_{\text{octa}} \text{Co}_{\text{tetra}} \text{-Co}_{\text{octa}} \text{ and higher Co–Co(O) coordination peaks from high- to low-temperature synthesis methods in the order Co}_3\text{O}_4\text{-SG > -MS > -PM > -MW-A > -MW-B > -HT-B} \) (Figure 3).

The amplitude decay in the FT\( k^{3}\chi(k) \) and WT spectra is correlated with a decrease of the coordination number or an increase in the mean-square disorder parameter \( \sigma^2 = \sigma_{\text{thermal}} + \sigma_{\text{static}} \) that is, Debye-Waller factors. Here, structural disorder arises from static disorder \( \sigma_{\text{static}} \) that is, crystal defects due to slightly different interatomic distances in the same coordination shell. The vibrational disorder \( \sigma_{\text{thermal}} \) is not crucial since the spectra have been all measured at the same temperature. Hence, the decline in the relative amplitude of high coordination peaks in the FT\( k^{3}\chi(k) \) and WT spectra provides a direct indication of the extent of crystalline long-range order around the cobalt centers. The results in Figure 3 and Table S2 suggest the existence of static disorder and the presence of Co and O vacancies in the structure of the cobalt oxides synthesized at low temperature, namely, \( \text{Co}_3\text{O}_4\text{-HT-B, -MW-B, -MW-A, and -PM} \). While the atomic coordination number \( n \) for \( \text{Co}_{\text{octa}} \text{-Co}_{\text{octa}} \text{Co}_{\text{tetra}} \text{-Co}_{\text{octa}} \text{ and higher Co–Co(O) coordination shells remains quite the same for Co}_3\text{O}_4\text{-SG, -MS, -PM, -BM, -TD, and -HT-A, the mean-square disorder } \sigma^2 \text{ of those oxides increases steadily} \) (Figures S1, S2, and Table S2). The static local disorder \( \sigma^2 \) increases most notably for \( \text{Co}_3\text{O}_4\text{-MW-A, -MW-B, and -HT-B} \). Additionally, for those oxide
materials, the atomic coordination number \( N \) of the Co–O, Co<sub>Oocta</sub>–Co<sub>Oocta</sub>, Co<sub>Tetra</sub>–Co<sub>Tetra</sub> and higher Co–Co(–O) coordination shells is slightly smaller than the corresponding values of the more crystalline samples Co<sub>3</sub>O<sub>4</sub>–SG, -MS, and -PM. The Co–O bond length of \( \approx 1.912 \) Å in Co<sub>3</sub>O<sub>4</sub>-MW-A is slightly larger with respect to the other oxides, suggesting lattice expansion and relaxation of Co–O bonds. These findings agree with results from PXRD and Raman spectra, in which Co<sub>3</sub>O<sub>4</sub>-MW-A, -MW-B, and -HT-B show lower intensity and broadened diffraction and Raman peaks due to the local structural dispersion of the Co and O atoms in the spinel structure (Figure 2a,c).

Figure 4a shows XANES spectra for as-synthesized Co<sub>3</sub>O<sub>4</sub>-SG, -MS, -PM, -MW-A, -MW-B, and -HT-B and those of the reference compounds Co<sub>2</sub>O<sub>3</sub> and LiCo<sub>2</sub>O<sub>2</sub>. The inset shows the calculated Co valence states, (b) zoom of changes in the pre-edge intensity of XANES spectra, and (c) zoom of the shifts of the Co K edge absorption edge to higher energies at \( \mu(E) = 0.5 \) of the normalized XANES spectra.

![Figure 4](image)

Figure 4. (a) XANES spectra of synthesized Co<sub>3</sub>O<sub>4</sub>-SG, -MS, -PM, -MW-A, -MW-B, and -HT-B oxides and reference compounds Co<sub>2</sub>O<sub>3</sub> and LiCo<sub>2</sub>O<sub>2</sub>. The inset shows the calculated Co valence states, (b) zoom of changes in the pre-edge intensity of XANES spectra, and (c) zoom of the shifts of the Co K edge absorption edge to higher energies at \( \mu(E) = 0.5 \) of the normalized XANES spectra.

The results in Figure 4b suggest that the cobalt distribution over the tetrahedral and octahedral sites, that is, the degree of inversion \( x \), could be slightly different among the synthesized oxides. Quantitative values of the degree of inversion \( x \) can be obtained from EXAFS fitting by weighting the amplitude of the scattering paths computed when the absorbing Co atom is located at the tetrahedral or octahedral sites. A single variable \( x \) corresponding to the degree of inversion was used as a fitting parameter multiplying the amplitude reduction factor \( S^0 \) of computed scattering paths from tetrahedral or octahedral sites. The calculated values for the degree of inversion \( x \) for all synthesized Co<sub>3</sub>O<sub>4</sub> spinel oxides are given in Table S2. The values of \( x \) range from \( x = 0.07 \pm 0.02 \) for Co<sub>3</sub>O<sub>4</sub>-SG to \( x = 0.18 \pm 0.02 \) for Co<sub>3</sub>O<sub>4</sub>-MW-B. These values agree with earlier reported data of inversion degrees \( x \) for spinel Co<sub>3</sub>O<sub>4</sub> oxides.\(^{78,79}\) The computed low \( x \) values for Co<sub>3</sub>O<sub>4</sub>-SG, -MS, -PM, and -HT-B suggest that those Co<sub>3</sub>O<sub>4</sub> oxides adopt the normal spinel structure. The slightly higher values of \( x \) for Co<sub>3</sub>O<sub>4</sub>-MW-A and -MW-B could suggest a slightly inverted spinel structure. While the energy position and line shape of the white line intensity in the XANES spectra are sensitive to experimental beam stability, the change in the white line intensity and the slight shift to lower energy (Figure 3a) further indicate the presence of structural disorder and an increase of the inversion degree \( x \). This result also suggests that the densities of unoccupied d-states and oxidation states of Co atoms are indeed different among the synthesized Co<sub>3</sub>O<sub>4</sub>-SG, -MS, -PM, and -HT-B oxides. These trends agree with those of PXRD and Raman spectra and indicate that low-temperature synthesis of Co<sub>3</sub>O<sub>4</sub> promotes the formation of a charge imbalance, Co and/or O vacancies, or unsaturated chemical bonds on the spinel surface structure.

X-ray Photoelectron Spectroscopy (XPS). XPS data for Co<sub>3</sub>O<sub>4</sub>-MW-B, -HT-B, -SG, and -PM are shown in Figure 5 together with those of the reference samples Co<sub>2</sub>O<sub>3</sub> and LiCo<sub>2</sub>O<sub>2</sub> for representative core-level spectra of Co<sup>2+</sup> and Co<sup>3+</sup> for all investigated cobalt oxides at \( \approx 780 \) eV (Figure 5a), which is in good agreement with literature reports.\(^{80}\) Whereas the peak positions for Co<sup>2+</sup> and Co<sup>3+</sup> are hard to distinguish, samples containing Co<sup>2+</sup> show an additional characteristic shake-up satellite emission at roughly 786 eV.\(^{81}\) The intensity of this satellite emission (inset of Figure 5a) can be used to assess the relative amount of Co<sup>2+</sup> present in the sample. Postcatalytic analysis of Co<sub>3</sub>O<sub>4</sub>-HT-B therefore reveals a small decrease in the relative Co<sup>2+</sup> amount (Figure 5S). By comparing the intensity of the satellite emission of the synthesized cobalt oxides with that of the reference compounds LiCo<sub>2</sub>O<sub>2</sub> and Co<sub>2</sub>O<sub>3</sub>, the following trend for the average Co valence states was derived: HT-B < PM < MW-B < SG. This trend is in good agreement with the XANES data shown in Figure 4a,c. Whereas the Co 2p<sub>1/2</sub>-core-level binding energies are similar for CoO and Co<sub>3</sub>O<sub>4</sub>, the shift in the kinetic energy of the L<sub>3VV</sub> Auger emission is considerable for different oxidation states.

As shown in Figure 4b, the XANES spectra of the synthesized oxides exhibit a characteristic pre-edge peak at about \( \approx 7709.6 \) eV, whose intensity slightly increases in the order Co<sub>3</sub>O<sub>4</sub>-MW-B > -MW-A > -HT-B > -PM > -SG. The pre-edge peak in XANES spectra is more intense for metal centers in tetrahedral symmetry and becomes broader and less intense for metal centers in octahedral coordination.\(^{77}\) Hence,
and the binding energies, the modified Auger parameters, is illustrated as diagonal lines. 83 The Auger parameter is insensitive to charging and particularly useful when comparing spectra of insulating samples with results from the literature. Modified Auger parameters from the National Institute of Standards and Technology (NIST) are given as references (Co3O4*, Co*, and CoO*) as indicated by the orange lines.80

The modified Auger parameters for the as-synthesized Co3O4-MW-B, -HT-B, and PM samples are on the same line with the Co3O4* reference. Interestingly, the measured CoIIO also coincides with this line, implying oxidation of the surface. The SG sample is closer to the LiCoIIIO2 line, which is in good agreement with the absence of a strong satellite emission as shown in Figure 5a. These findings correlate well with the previous spectroscopic measurements, showing the same trends, namely, lower average oxidation states for samples synthesized at lower temperatures.

**Water Oxidation Performance of Co3O4 Samples from Different Preparative Routes.** The water oxidation performance of Co3O4 samples synthesized by nine different methods was tested using the three most widely applied approaches, namely, photocatalytic, electrochemical, and chemical oxidation methods, together with the respective BET surface area and the mean-square disorder parameter σ². For the photocatalytic oxidation, a standard [Ru(bpy)3]²⁺/S2O8²⁻ protocol was used with a borate buffer (pH 8.5). Electrocatalytic activity is compared by the potentials vs reversible hydrogen electrode (RHE) at 1 mA/cm² in 1 M KOH, and chemical oxidation was tested in 146 mM cerium(IV) ammonium nitrate (CAN).

Figure 6 shows a quite significant difference in activity. The samples synthesized at lower temperatures generally show higher OER activity, with the hydrothermally synthesized Co3O4-HT-B demonstrating the highest activity with an O2 yield of 77.7 ± 6.4% at 203 m²/g, compared with the samples obtained at high temperatures where the least active catalyst is Co3O4-MS with 12.4 ± 0.4% at a surface area of only 2 m²/g. This goes hand in hand with the observed high surface areas of MW-A (99 m²/g), MW-B (146 m²/g), and HT-B (203 m²/g). However, HT-A and PM, which exhibit relatively low surface areas, also show higher performance than most of the samples. Among the high-temperature samples, Co3O4-MW, -BM, and -SG show a trend toward higher activity upon increasing surface area. Co3O4-TD is again an exception with a rather high activity of 46.9 ± 4.6% for its comparably low surface area of 11 m²/g. Note that the disorder among the samples follows a related trend related to the surface area. No clear correlation between the activity and either of the parameters surface area, disorder, or valence state can be seen in photocatalytic water
oxidation. The general photocatalytic performance trend reveals a higher activity for materials synthesized through low-temperature hydrothermal or precipitation methods (≤180 °C) than for materials synthesized at high temperatures (≥400 °C) (CoOx@TD being the above-mentioned exception). Consequently, the selected synthetic method exerts a clear effect on photocatalytic water oxidation activity.

**Electrocatalytic Performance.** Electrochemical measurements were performed in a three-electrode setup, using Ag/AgCl as the reference electrode and Pt as the counter electrode. Ag/AgCl is still widely applied as the reference electrode for measurements in basic media (for example, 1 M KOH), when keeping in mind that minor stability issues can occur due to silver oxide formation in basic conditions. We performed control experiments using a Ag/AgCl reference electrode to ensure that such effects did not affect the required accuracy of our measurements.\(^85\)–\(^87\) Considering the recently shown instability of Pt under certain conditions, this occurs mainly in acidic environments and affects the water reduction half reaction rather than the oxygen evolution process. Further discussions can be found in the SI and in Figure S10a.\(^88\)–\(^92\) To evaluate the electrocatalytic water oxidation performance, the spinel samples were coated on fluorine doped tin oxide (FTO), and cyclic voltammetry as well as chronoamperometry was performed, first stepwise from 0.45 to 0.65 V versus Ag/AgCl and then for 2 h at 0.6 V. The electrodes were investigated before and after these measurements with scanning electron microscopy imaging, Raman spectroscopy, and PXRD (Figures S8–S10). All of these characterizations did not show notable changes of the electrodes. Only in the PXRD patterns did the postcatalytic samples show increased intensity of the FTO peaks, which is most likely due to partial detachment of the catalyst from the electrode, but not arising from intrinsic changes of the catalyst itself. No clear trend is apparent from the cyclic voltammograms, where all samples showed an onset potential in the range of 1.49–1.64 V versus RHE with significant standard deviations of 0.03 V (see Figure S8). The only remarkable feature is that CoOx-MS, with an overpotential of 1.64 V versus RHE, is outperformed clearly by all other materials. For a better internal comparison of the obtained materials, stepwise chronoamperometry was conducted to eliminate the diffusion current, therefore representing the catalytic activity more reliably. The potentials at 1 mA/cm\(^2\) are determined from Figure S11 and compared in Figure 6. Other than in photocatalytic tests, even from these more accurate measurements, no clear influence on the electrocatalytic performance is evident. All potentials at 1 mA/cm\(^2\) are in the range of 1.57–1.62 V versus RHE with a comparatively large error of 0.024 V. This indicates that the differences among the materials, such as in surface area, disorder, or oxidation state, are less important for electrocatalytic water oxidation, that is, the influence of the synthetic method is rather negligible here. As the postcatalytic investigations still show the presence of CoO\(_x\) (see SI, pre- and postcatalytic analyses), the observed leveling may point to a reversible precatalytic formation of a thin shell of CoO\(_x\)(OH)\(_y\) in line with the in situ XRD/XAS study of Dau and Strasser et al. describing the reversible formation of a catalytically active subnanometer CoO\(_x\)(OH)\(_y\) layer containing di-μ-oxo-bridged Co\(^{3+}/4+\) ions.\(^93\) A related in situ study by Chen et al. on CoO\(_x\)(@CoO nanocubes supported the intermediate formation of active α- and β-CoOOH thin layers.\(^94\) In light of these findings, pristine surface compositions and structures of such oxides would indeed be relativized to a large extent in electrochemical tests.

**Chemical Oxidation Performance.** Chemical water oxidation was tested with the strong one-electron oxidant cerium-IV ammonium nitrate (CAN) with an \(E^o\) of 1.7 V versus NHE.\(^94\),\(^95\) CAN-assisted oxidation is a relatively simple and straightforward protocol for WOC assessment since the kinetics are driven in one-electron steps and commercially available \(O_2\) sensors can be used. However, CAN is only sufficiently stable at low pH values of typically 0.9, which limits its applicability.\(^96\) Even though chemical and photochemical water oxidation tests are thus performed at very different pH values, their “overpotentials” for water oxidation correspond to comparable \(E^o\) at the given pH values.\(^14\) In our case, water oxidation was tested with a standard method, measuring \(O_2\) production by a luminescent dissolved oxygen (LDO) electrode with results between 5 × 10\(^{-2}\) and 10\(^{-2}\) mmol oxygen/mg catalyst. CoO\(_x\)-HT-B was the most active catalyst (1.05 × 10\(^{-2}\) mmol oxygen/mg), and CoO\(_x\)-MS showed the lowest activity (6.45 × 10\(^{-4}\) mmol oxygen/mg, see Figure 6), as observed for photocatalytic oxidation. Despite this similarity and the comparable “overpotentials”, the activities of the other cobalt oxides vary drastically between both test methods. In contrast to the photochemical oxidation, the activities for the chemical oxidation display the expected correlations with the material parameters. The activity increases clearly with the BET surface area. Likewise, the increasing disorder among the sample series results in continuously higher activity. As BET surface area and disorder show similar trends, both being linked to the preparative history, a reasonable further narrowing to one key performance parameter is not possible within the present data set. Additionally, the lower general oxidation states derived from XANES and XPS data, indicating excess Co\(^{2+}\) associated with oxygen vacancies, could be a key performance parameter. Generally, samples synthesized at lower temperatures show higher activities than the high-temperature samples, such as CoO\(_x\)-MS, -BM, and -SG (Figure 6).

**Trends in WOC Assessment.** All in all, quite different performance trends were observed for CoO\(_x\) WOCs when investigated with all three catalytic methods. This agrees with the first fundamental investigation along these lines by Stahl et al.\(^14\) comparing different manganese oxide types for photocatalytic, chemical, and electrocatalytic water oxidation as well as with subsequent studies of Ding et al.\(^97\) on doped iron-based oxides. The present study newly demonstrates that even the catalytic activity of a single material type can differ widely between test methods when it undergoes different preparative histories. While Antonietti and Driess et al.\(^41\) tailored the particle size of cobalt oxides with related synthetic methods and found the efficiency of photo- and electrocatalytic water oxidation of CoO\(_x\) nanoparticles to depend on the available surface area, our previous studies on CoO\(_x\) hydrothermal growth mechanisms indicated that the surface area is not by all means the decisive performance parameter.\(^13\)

While photochemical and chemical oxidation are both molecular processes, they were found to respond differently to the involved material parameters, that is, the preparative method exerts a clear influence on the WOC activity. Surface area, oxidation state, and disorder were identified as the most important parameters for the chemical oxidation performance. In contrast, no such trend for these parameters could be found for the photochemical oxidation. However, in both test
methods, Co3O4 samples synthesized at higher temperatures generally show lower activity than those obtained at notably lower synthesis temperatures. As for electrochemical water oxidation, no parameter dependence with respect to surface area, particle size, disorder, etc. emerged, so that the choice of the synthesis method exerted a negligible effect on the electrocatalytic performance.

**CONCLUSIONS**

In this work, a comprehensive three-step strategy using spinel-type Co3O4 water oxidation catalysts (WOCs) as a model system was newly applied to investigate the complex parameter space of preparative history, material properties, and the resulting performance as a function of the applied catalytic driving force. To this end, nine different synthetic approaches to Co3O4 were first performed, covering a wide spectrum of low- and high-temperature methods. Next, key physical and surface properties of the as-synthesized products were compared, such as oxidation states, crystallinity, disorder, and particle size. Finally, this spectrum of cobalt oxide materials was compared with respect to their WOC activities in the three most widely applied test methods, namely, photocatalytic, electrocatalytic, and chemical water oxidation.

The Co3O4 samples synthesized at lower temperatures show higher disorder, as determined from EXAFS fitting and in line with Raman spectroscopy results. These more disordered samples also contain lower fractions of Co(III) than those exhibiting a higher degree of crystallinity, as evident from XPS and XANES data. Generally, cobalt oxides synthesized at low temperatures (<180 °C) show higher water oxidation activities in chemical and photocatalytic tests than those obtained at higher temperatures. Chemical oxidation with CAN brought forward the clearest correlation between increasing catalytic activity and higher surface area/disorder along with lower average cobalt oxidation states. In contrast, the electrochemical water oxidation activity is quite insensitive to variations in the material properties. Surprisingly, no clear photocatalytic activity trends were observed for the Co3O4 sample spectrum. All in all, we demonstrate that the preparative history exerts a crucial influence on the material properties of Co3O4 WOCs. These distinct synthesis-dependent properties give rise to significant activity differences in chemical and photochemical assays. Our systematic study shows that acquiring comprehensive synthetic insight is a fundamental prerequisite for any further properties–performance relationships. We here show their striking complexity for an apparently straightforward binary oxide system. In the long term, control over the entire parameter space of preparation, properties, and performance will require machine learning approaches to expedite the optimization of a wide spectrum of catalytic and other functional materials.

**EXPERIMENTAL SECTION AND METHODS**

**Synthetic Procedures.** *Hydrothermal Synthesis (HT-A).* For the hydrothermal synthesis of Co3O4, 0.24 g of urea (4 mmol) and 0.233 g of Co(NO3)2·6H2O (0.82 mmol) were dissolved in 10 mL of H2O (30 wt %) solution under vigorous stirring. The homogeneous reaction solution was transferred to a 15 mL poly(tetrafluoroethylene) (PTFE)-lined stainless steel autoclave and heated to 150 °C (4.5 °C/min). The holding temperature was maintained for 3 h. The autoclaves were cooled down rapidly under cold running water (10 °C) for 8 min. The black precipitate was purified by centrifugation/resuspension (5000 rpm, 8 min, 2 × H2O and 2 × EtOH) and dried at 78 °C for 16 h in air.

**Alternative Hydrothermal Synthesis (HT-B).** The alternative hydrothermal synthesis was carried out according to the following procedure:79 291 mg of Co(NO3)2·6H2O (1 mmol) and 42.5 mg of NaNO3 (0.5 mmol) were dissolved in 15 mL of H2O. After 10 min of stirring, 15 mL of NH3 (25%) solution was slowly added, and after 10 more minutes of stirring, 1.5 mL of H2O2 (30 wt %) solution was added. The reaction solution was transferred to a 15 mL PTFE-lined stainless steel autoclave and heated to 140 °C (4.5 °C/min). The holding temperature was maintained for 6 h and then cooled to room temperature naturally. The black precipitate was purified by centrifugation/resuspension (5000 rpm, 8 min, 2 × H2O and 2 × EtOH) and dried at 78 °C for 16 h in air.

**Microwave Hydrothermal Synthesis (MW-A).** For the microwave hydrothermal synthesis of Co3O4, 1.8 mmol of Co(NO3)2·6H2O was dissolved in 15 mL of H2O and the pH was adjusted to 11 with NH3 (25%) solution. The resulting dispersion was filled into a 50 mL Teflon liner, which was closed and fixed inside a frame before introducing into the microwave. Reactions were carried out in a MARS microwave (CEM Corporation). The synthesis was conducted by controlling the temperature: 30 min ramping to 180 °C and then holding this temperature for 60 min under constant stirring. The temperature and pressure were measured from the reference vessel, which was equipped with appropriate sensors. After letting the dispersions cool down to room temperature, the product was separated by centrifugation and washed with H2O.

**Microwave Alternative Hydrothermal Synthesis (MW-B).** First, 100 mM Co(NO3)2·6H2O and 50 mM NaNO3 were dissolved in 5 mL of H2O. Then, 5 mL of NH3 (25%) solution and 0.5 mL of H2O2 (32 wt %) were added before sealing the solution in the corresponding vessels as described in the above section. The reaction was carried out at 140 °C for 1 h after 30 min of ramping time.

**Mild Oxidative Synthesis/Precipitation Method (PM).** The nitrate-salt-mediated precipitation method was carried out according to a previously reported procedure.7 NaNO3, (15 g, 176 mmol) was added to a 50 mL two-necked round-bottom flask, equipped with a water-cooled reflux condenser containing 25 mL of NaOH solution (0.3 M). The reaction mixture was heated to 95 °C, and an aqueous solution of Co(NO3)2 (5.0 mL, 1.0 M) was added within 1 min, which led to instantaneous precipitation. Throughout the precipitation and aging period, the reaction mixture was stirred vigorously and purged with air while keeping the temperature constant at 95 °C for 16 h. Afterward, the suspension was cooled to room temperature naturally under ambient conditions. The black precipitate was purified by centrifugation/resuspension (5000 rpm, 8 min, 2 × HCl (2 M), 1 × H2O and 1 × EtOH) and dried at 78 °C for 16 h in air.

**Thermal Decomposition (TD).** For the synthesis of Co3O4 through thermal decomposition, Co(NO3)2·6H2O was added to a crucible, heated in a muffle furnace to 450 °C (4.5 °C/min), and kept at this temperature for 3 h. Afterward, the product was cooled to room temperature naturally.

**Ball Milling (BM) and Thermal Decomposition.** Co(NO3)2·6H2O was ground in a planetary ball mill (Retsch) at a speed of 500 rpm for 2 h. The ball-milled powder was...
calcined in air at 450 °C for 1 h to obtain larger Co₃O₄ nanoparticles.

**Sol–Gel (SG).** A variation of the sol–gel method from ref 98 was applied: 1.8 mmol Co(NO₃)₂·6H₂O and 2.7 mmol citric acid were dissolved in 25 mL of H₂O. The solution was heated up slowly while stirring until a gel was formed. It was heated up to 400 °C for 1 h, transferred into a ceramic crucible, and then heated again to 700 °C for 10 h, yielding Co₃O₄.

**Molten Salt (MS) Method.** Co(NO₃)₂·6H₂O (0.291 g, 1 mmol) was mixed with LiNO₃ (6.695 g, 100 mmol), ground, and transferred to an aluminia crucible. The crucible was put into a muffle furnace, heated to 400 °C (12.6 °C/min), and kept at this temperature for 30 min. Afterward, the mixture cooled down to room temperature naturally and was washed (2 × H₂O and 1 × EtOH) and dried at 78 °C for 16 h in air.⁵⁰

**Catalytic Measurements. Photocatalytic Tests.** Photocatalytic water oxidation tests were performed using a standard 2+[Ru(bpy)₃]²+/S₂O₈²⁻ protocol.¹³ Photocatalytic reaction suspensions were handled in a dark environment while being shielded from light. According to the protocol, Co₂O₃ photocatalyst (2.00 mg, 8.3 mmol), Na₂S₂O₈ sacrificial electron acceptor (9.5 mg, 5 mM), and [Ru(bpy)₃]Cl₂·6H₂O photosensitizer (6.0 mg, 1 mM) were mixed with borate buffer (8 mL, 80 mM, pH 8.5) in a 10 mL headspace glass vial. The glass vial was subsequently sealed gastight with a rubber septum (PTFE) and an aluminum crimp cap and sonicated for 3 min. To remove all of the oxygen before starting the test, the suspension was degassed through purging with helium (purity 5.0) for 10 min. Afterward, the catalytic suspension was illuminated with a 460 nm high flux light-emitting diode light (26.1 mW/cm², Rhopoint Components Ltd.) under constant stirring (1200 rpm) for 25 min. For evaluating the amount of evolved oxygen, a 100 μL gas sample was taken from the headspace with a gastight microliter syringe (Hamilton-1825RN) and injected into the gas chromatograph (GC). A headspace with a gastight microliter syringe (Hamilton-1825RN) and injected into the gas chromatograph (GC). Afterward, the mixture cooled down to room temperature naturally and was washed (2 × H₂O and 1 × EtOH) and dried at 78 °C for 16 h in air.⁵⁰

**Chemical Water Oxidation.** The standard CAN method was used to evaluate the chemical water oxidation activity of the catalysts.⁵⁹ With a standard potential of about 1.7 V versus NHE, CAN can be a suitable one-electron oxidant to promote the water oxidation. CAN (2 g) was dissolved in Milli-Q water (40 mL), and the solution was degassed with argon. The respective catalysts (2 mg each) were added, and the oxygen evolution was recorded by a luminescent dissolved oxygen (LDO) sensor in the stirred solution for about 45 min. The highest obtained value was used for the evaluation. A Hach HQ40D multimeter with an LDO 101 sensor was used for oxygen determination.

**Electrochemical Tests.** Electrochemical measurements were carried out in 1 M KOH, using a Ag/AgCl reference electrode and a Pt counter electrode. First, cyclic voltammetry cycles from 0 to 0.7 V versus reference with 0.005 mV step size were measured, prior to conducting chronoamperometry. For comparison, only the second cycle was considered upon data evaluation. The potential was stepwise increased starting from 0.45 to 0.65 V in 0.01 V steps and held for 5 min each to eliminate diffusion currents. The stabilized current after 5 min was used for further evaluation. After the steps, a potential of 0.6 V versus the reference electrode was applied for 2 h for stability tests. Electrochemical measurements were carried out with a Bio-Logic SAS SP-150 Potentiostat. As the reference electrode, an Aldrich glass reference electrode Ag/AgCl with 3 M KCl and as the counter electrode, a Pt foil were used. The working electrodes were produced by dispersing 2 mg of the catalyst in 100 μL of H₂O, applying 40 μL of this dispersion on 1 cm² FTO, and drying the electrodes at 80 °C for 30 min before covering with 10 μL of Nafion 1% solution.

**Materials and Methods.** Ultrapure H₂O (18.2 MΩ) was generally used for synthesis (Merck, Milli-Q Type 1 Ultrapure Water Systems). All chemicals and solvents were purchased from commercial suppliers: CoO (Aldrich, ≥99.99% metals basis), LiCoO₂ (Alfa Aesar, 99.5% metals basis), Co(NO₃)₂·6H₂O (Sigma-Aldrich, 99.999% trace metal basis), [Ru(bpy)₃]Cl₂·6H₂O (Sigma-Aldrich, 99.95%), Na₂S₂O₈ (Sigma-Aldrich, 99.0%), H₂O₂ 30 wt % in H₂O (Sigma-Aldrich, ACS Reagent), urea (Sigma-Aldrich, 98%), NaNO₃ (Sigma-Aldrich, ≥99.0%), NaOH (Acros Organics, 97%), LiNO₃ (Sigma-Aldrich, ReagentPlus), ammonia solution 25% (Merck, for analysis), ethanol (VWR Chemicals, absolute), citric acid (Merck, anhydrous for synthesis), KOH (Honeywell, pellets, extra pure), HCl (Fluka Analytical), Nafion perfluorinated resin solution 5 wt % in a mixture of lower aliphatic alcohols, and water (Sigma-Aldrich).

Powder X-ray diffraction (PXRD) patterns were recorded with a STOE STADI P diffractometer in the transmission mode (flat-plate sample holder, Ge monochromator, and Mo Kα₁ radiation) using a position-sensitive microstrip solid-state detector (MYTHEN 1K). Raman spectroscopy was performed with a Renishaw inVia Qontor confocal Raman microscope equipped with a diode laser (785 nm). Gas chromatography (GC) measurements were recorded with Agilent Technologies 7820A equipped with a thermal conductivity detector and a 30 m × 0.53 mm packed HP molecular sieve column with a 50.0 μm film and He carrier gas (purity 6.0). Nitrogen sorption isotherms were recorded with a Quantachrome Quadrasorb SI porosimeter at 77 K after degassing at 100 °C for 20 h under vacuum. The Brunauer–Emmett–Teller (BET) model was applied for adsorption branch points (0.05 < p/p₀ < 0.3) to calculate the apparent surface area. Transmission electron microscopy (TEM) images were taken with JEOL JEM-1400 Plus equipped with a JEOL CCD camera Ruby (8 M pixel) and a LaB₆ crystal as an emitter (120 kV). X-ray absorption spectroscopy XANES and EXAFS at the Co K edge on solid powder samples dispersed in cellulose of the synthesized Co₃O₄ oxides and reference samples CoO₃·LiCoII(OH)₃ was carried out at the European Synchrotron Radiation Facility, Swiss-Norwegian Beamline BM31, Grenoble-France. The storage ring was run in the top-up mode (average current 40 mA). The X-ray beam was collimated using a Si-coated mirror, and energy was scanned using a double crystal Si[111] monochromator. Measurements were performed at room temperature using a three-ionization chamber configuration in the transmission mode using a 13-element Ge detector. For energy calibrations, spectra of a metal Co foil were measured simultaneously at the second ionization chamber. The measured EXAFS spectra k²χ(k) were extracted by data reduction, absorption edge energy calibration, and background subtraction as implemented in ATHENA.⁶⁹ The spectra were reduced in the range Δk ≈ 3–14 Å⁻¹ and Fourier-transform to FTk²χ(k) into the real-space interval of ΔR ≈ 0–6 Å. To calculate main values for interatomic distances, coordination numbers, and Debye–Waller factors σ nonlinear least-squares fitting of the experimental FTk²χ(k) spectra was carried out.
by ARTEMIS\textsuperscript{99} using atomic clusters of Co\textsubscript{3}O\textsubscript{4} (ICSD code 27498), generated by ATOMS\textsuperscript{99} as implemented in IFEFFIT.\textsuperscript{100} The amplitude and phase shifts for single and multiple scattering paths were calculated using FEFF6.\textsuperscript{100} X-ray photoelectron spectroscopy (XPS) was conducted using a Physical Electronics (PHI) Quantum 2000 spectrometer featuring monochromatic Al K\textsubscript{x} radiation, generated from an electron beam operated at 15 kV and 35.8 W. The energy scale of the instrument was calibrated using Au and Cu reference samples. The analysis was conducted at 1 e\textsuperscript{–}8 mbar, with an electron take-off angle of 45\degree and a pass energy of 23.5 eV for all samples. Charge compensation during the measurement was achieved using a low-energy electron source. The acquired spectra were then aligned using the main (C 1s) component of the C 1s core-level emission. The modified Auger parameter was calculated by adding the kinetic energy of the Co L3VV and Co 2p\textsubscript{3/2} binding energies.

\section*{ASSOCIATED CONTENT}

\subsection*{Supporting Information}

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.9b01677.

Additional characterization and catalytic water oxidation measurements of the as-synthesized Co\textsubscript{3}O\textsubscript{4} materials (PDF)

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L.R. and K.L. contributed equally to this work. The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

\section*{Notes}

The authors declare no competing financial interest.

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