Large-Scale Production of Carbon-Supported Cobalt-Based Functional Nanoparticles for Oxygen Evolution Reaction

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A series of Co-based nanoparticles supported on activated carbon was synthesized by using waste tea leaves as a template as well as a sustainable carbon source. The crystal structure of the Co particles was adjusted by post-treatments with H_2O_2, ethanol vapor, and H_2, which result in Co_3O_4, CoO, and metallic Co phases, respectively. After these different treatments, the composite materials consist of small Co-based nanoparticles with an average crystallite size of 6–14 nm supported on activated carbon with apparent specific surface areas up to 1065 m² g⁻¹. Correlations between the structure of the materials and their activity for the oxygen evolution reaction (OER) were established, whereby the post-treatment with ethanol vapor was found to yield the most effective electrocatalyst. The material shows good stability at 10 mA cm⁻² over 10 h and reaches a mass activity of 2.9 A mg^Co⁻¹, which is even higher than pristine ordered mesoporous Co_3O_4. The superior electrocatalytic performance is ascribed to a high dispersion of Co-based nanoparticles and the conductivity of the activated carbon that facilitate the charge transport.

Introduction

Supported Co-based materials are important catalysts in many chemical reactions. For example, petrochemical processes, such as Fischer-Tropsch synthesis,[1,2] water-gas shift reaction,[3,4] higher alcohol synthesis,[4] hydrodesulfurization,[5] (selective) hydrogenation,[6–8] and hydrodeoxygenation,[9] rely on Co-based catalysts, mostly supported on oxide materials. Furthermore, electrochemical reactions are increasingly attracting attention as a promising way to store and utilize renewable electrical energy in form of H_2, thus reducing society’s dependency on fossil fuels.[10] In this regard, Co is a promising element to replace rare noble metals such as Pt and Ir as catalysts for the hydrogen oxidation reaction (HOR) and oxygen reduction reaction (ORR) in fuel cells,[11,12] and the hydrogen evolution reaction (HER), and oxygen evolution reaction (OER) in electrolyzers.[13,14] These catalytic processes benefit from conductive carbon supports that are crucial to achieve sufficient charge transport in the composite material for better performance. Consequently, for the above-mentioned electrochemical reactions, the carbonaceous support should stabilize the Co-based nanoparticles, provide a high specific surface area for the catalytically active component, and improve the electrical conductivity of the composite material.

However, the synthesis of uniformly sized Co-based nanoparticles supported on carbon materials can be time-consuming and complicated. A simple wet impregnation of Co salts on activated carbon often results in broad particle size distributions with some proportion of larger particles.[15,16] Supported metal nanoparticles with uniform particle size distributions could be obtained via ordered mesoporous carbon materials due to pore confinement in their well-defined pore system, however, this requires multiple synthetic steps and several days of lab-work.[17–20] Recently, the methods for the preparation of carbon-supported Co-based nanoparticles were extended by the simple pyrolysis of metal-organic frameworks (MOFs) as single precursors[21,22] although both of these approaches yield the desired highly dispersed small nanoparticles of the active species, the synthesis efforts are undeniable. The production of organic polymers as soft-templates for the ordered mesoporous carbon materials or the synthesis of organic linkers for the MOFs is very time-consuming. The following pyrolysis of the organic materials to obtain the carbon-supported transition metal-based nanoparticles makes those synthesis methods very costly and inefficient from an economical point of view. This also leads to poor scalability with respect to the catalyst yield, which limits their large-scale applications.

A more sustainable and scalable method for the production of transition metal-based nanoparticles supported on carbon is using biomass-based templates like plant leaves.[23,24] As an example for an abundant carbon source, over 5 Mt of tea leaves are produced per year.[25] The waste of those tea leaves can be recycled and valorized for catalyst production. Further, the use of biomass as carbon source brings the advantage of direct incorporation of hetero-elements like N, P, and S into the final carbon material that proved to be beneficial for electrocatalytic...
applications.\textsuperscript{35–38} The advantage of leaves over conventional activated carbons as support is that during the impregnation with the metal salt solution, the natural transport network of the leaves for water and nutrients is utilized to attain a high dispersion of transition metal ions in the carbon material.\textsuperscript{[39]} When the impregnated plant leaves are pyrolyzed under an inert atmosphere, carbonization of the biomass takes place and results in transition metal nanoparticles supported on hetero-element substituted carbon materials.\textsuperscript{[40–42]} On the downside, due to the reductive properties of carbon under heat treatment, this approach often leads to highly reduced transition metal-based nanoparticles. Thus, it is challenging to obtain transition metal species with higher oxidation states because thermal oxidation of the nanoparticles under air can combust the carbon support. Nevertheless, controlling the oxidation state of the nanoparticles is desirable to adjust the catalytic performance of the material for the respective reactions. For example, highly oxidized Co\textsuperscript{3+–4+} species are assumed to be the active sites for OER under alkaline conditions (4 OH\textsuperscript{−}→O\textsubscript{2} + 2 H\textsubscript{2}O + 4 e\textsuperscript{−}).\textsuperscript{[43]} Furthermore, the pyrolysis of biomass usually does not lead to carbon materials with the desired high surface area. One way to increase the apparent specific surface area of carbon materials is the well-established activation with KOH.\textsuperscript{[44]} Under thermal treatment, KOH reacts with the carbon from the biomass leading to gaseous products like CO and CO\textsubscript{2}, thus creating pores and increasing the apparent specific surface area.\textsuperscript{[45,46]}

Herein, a facile and versatile synthesis procedure is presented to produce carbon-supported Co-based nanoparticles on a large scale whereas tea leaves are used as both, a template and a sustainable carbon source. The crystal structure and oxidation state of the cobalt nanoparticles are selectively adjusted (including Co\textsubscript{3}O\textsubscript{4}, CoO, and Co) by treating the material with either H\textsubscript{2}O\textsubscript{2}, ethanol vapor, or H\textsubscript{2}. The effects of these post-treatments on the textural and structural properties of the materials are thoroughly investigated and a structure-activity correlation for the OER is established.

### Results and Discussion

Herein, a versatile, cheap, and scalable synthesis procedure for activated carbon-supported nanoparticles is developed by using tea leaves as a sustainable carbon source as well as a template. The tea leaves were impregnated with Co-(NO\textsubscript{3})\textsubscript{2}·6 H\textsubscript{2}O, urea, and KOH followed by pyrolysis at 600 °C under an Ar atmosphere. Under these conditions, the cobalt precursor decomposes to its metal and metal oxide counterparts, and the tea leaves got carbonized and lost roughly 60% of their initial mass due to the release of pyrolysis oil and activation by KOH. Previous studies indicated that biomass wastes like spent tea leaves and coffee waste can be used as hard-templates to prepare metal oxide nanoparticles since metal precursors can be converted to their metal oxide counterparts within the confined pores of the templates before their combustion under air.\textsuperscript{[47,48]} When instead the pyrolysis is carried out under an Ar flow, the tea leaves are converted to carbon and this leads to the formation of cobalt nanoparticles supported on activated carbon. Herein, cobalt has a loading of roughly 20 wt.%. However, by simply changing the ratios of metal precursors and tea leaves, the loading of the nanoparticles can be easily varied. With this procedure, roughly 2 g of catalyst could be obtained (which is one-third of the mass of the precursors) and it has the potential to be easily scaled up.

It was targeted to control the crystal structure as well as the oxidation state of the cobalt nanoparticles and to tune the surface structure of the carbon support by choosing a proper post-treatment of the resulting material with either H\textsubscript{2}O\textsubscript{2}, ethanol vapor, or H\textsubscript{2}. The synthetic protocol of the process is illustrated in Scheme 1. To verify that the adjustment of the crystal structure and oxidation state of the Co species was successful, the crystal phases of the nanoparticles were determined by XRD patterns (Figure 1). For the as-made-CoO\textsubscript{2} sample, the washing step with water (to remove the alkaline potassium salts) led to the hydrolysis of the Co\textsuperscript{2+} ions to form layered double hydroxide Co(OH)\textsubscript{2} in the α- and β-phase (β-phase pdf 2 no. 01-074-1057).\textsuperscript{[49]} In those materials, the Co\textsuperscript{2+} ions are octahedrally coordinated by OH\textsuperscript{−} ions and are arranged in a hexagonal layered structure. The difference in the α- and β-
Co(OH)₂ polymorphs is a larger interlayer distance of the double hydroxide layers in the α-phase than in the β-phase due to incorporated anions between the several layers in the α-phase. A small proportion of the Co₂O₄ spinel structure (pdf 2 no. 00-42-1467) was observed as well, in which Co²⁺ ions are tetrahedrally and Co³⁺ ions are octahedrally coordinated by O²⁻ ions. With the Scherrer method, the size of the β-Co(OH)₂ crystallites was determined as about 28 nm. A detailed comparison of the crystal structures and other parameters is provided in Table 1.

To convert the Co(OH)₂ nanoparticles into Co₃O₄, oxidation with H₂O₂ with subsequent drying at 110 °C was chosen. Upon contact with the Co-containing composite material, the H₂O₂ decomposes most likely into *OH and OOHradicals as it is reported in the literature. These radicals can then oxidize the Co(OH)₂ into pure Co₃O₄ under milder conditions than conventional thermal oxidation with O₂. That relatively mild oxidation prevents the undesired decomposition of the activated carbon support. Additionally, the crystallite size for this phase was reduced to 12 nm, indicating segregation of the Co(OH)₂ crystallites during the treatment. For a mild reduction of the as-made-Co₃O₄ composite material, it was treated under ethanol vapor at 270 °C. In the presence of cobalt oxide, the ethanol decomposes into acetaldehyde and H₂ that then can transform the Co(OH)₂ and Co₃O₄ into pure cubic rock-salt structured CoO (pdf 2 no. 00-09-0402). In this structure, the Co²⁺ ions are octahedrally coordinated by 6 O²⁻ ions. Remarkably, the mean crystallite size of the pure CoO phase was determined with the Scherrer method to be only around 6 nm, which is much smaller than for the as-made-Co₃O₄ and H₂O₂-Co₃O₄ samples. This indicates that the ethanol vapor treatment forced rearrangements of the crystallites and caused a reduction of their sizes.

As seen in Figure 1, for the sample treated under H₂ atmosphere, the Co-based nanocrystallites were completely reduced to the cubic and hexagonal phase of metallic Co (pdf 2 no. 00-15-0806 and 01-89-4308). Further, small reflections of CoO are also observed originating from the passivation of the metallic nanoparticles under 1% O₂ in Ar after the reduction. A determination of the crystallite size with the Scherrer method was not possible for this sample because the reflections were not well resolved from each other. However, the observation of sharper reflections compared to the EtOH-CoO sample indicates the formation of larger metallic cobalt nanoparticles. The XRD study proved that it was possible to selectively adjust the oxidation state and consequently the crystal phase of the Co-based nanoparticles between Co²⁺, Co³⁺, and Co²⁺/³⁺. All patterns exhibit a broad hump between 20-30° 2θ corresponding to XRD-amorphous carbon, indicating that there is no graphitization of the carbon material over a long-range occurring under the chosen conditions.

To identify the Co loading for each sample, the elemental compositions of the materials were determined with bulk SEM-EDX measurements (Table S1). The as-made-Co₃O₄ sample and the EtOH-CoO sample both contain around 18 wt.% of Co, which falls into the range of the theoretically expected 20 wt.%. For the H₂O₂-Co₃O₄ sample, the Co amount drops to 15 wt.% which is attributed to the increase of the oxygen content in the material from 18 wt.% (as-made-Co₃O₄) to 25 wt.%. The opposite effect is observable for the H₂-Co sample. Here, oxygen is removed under the reductive treatment (8 wt.%) increasing the share of carbon (70 wt.%) and Co (21 wt.%) in the material. Overall, the Co loadings for all samples are more or less in a similar range indicating no excessive loss of carbon or Co during the post-treatment procedures. The small changes in Co

![ChemCatChem - XRD patterns of the samples](image)

**Figure 1.** XRD patterns of the samples as-made-Co₃O₄ (black), H₂O₂-Co₃O₄ (red), EtOH-CoO (blue), and H₂-Co (pink).

### Table 1. Co crystal phases, domain sizes, apparent specific surface areas, I/I° ratios, current densities, and overpotentials of the samples as-made-Co₃O₄, H₂O₂-Co₃O₄, EtOH-CoO, and H₂-Co.

| Crystal Phase | as-made-Co₃O₄ | H₂O₂-Co₃O₄ | EtOH-CoO | H₂-Co |
|---------------|--------------|------------|----------|-------|
| Co-based Domain Size [nm] [a] | 28 [b] | 12 | 5.9 | 6 |
| Apparent Specific Surface Area [m² g⁻¹] | 758 | 595 | 929 | 1065 |
| I/I° Ratio [a] | 5.4 | 5.9 | 5.1 | 4.7 |
| Current Density@1.7 V vs. RHE [mA cm⁻²] | 33 | 30 | 65 | 66 |
| Overpotential@10 mA cm⁻² [mV] | 407 | 406 | 380 | 377 |

[a] Crystallite size calculated with the Scherrer equation of at least 3 reflections of the pattern assuming a shape factor of 1. [b] Crystallite size of β-Co(OH)₂ from the reflections at 32.5, 51.4, and 61.6° 2θ. [c] Average particle size determined from TEM micrographs. [d] Mean value of 18 spectra from different spots.
loading can be explained by the introduction or removal of oxygen in the samples with the different post-treatments. It should be noticed that the absolute amount of carbon and oxygen determined with EDX is not reliable because carbon and oxygen are light elements that do not release electrons easily. Further, the carbon content in the sample is probably overestimated due to the carbon-containing specimen holder. Consequently, the amounts of Co and oxygen are underestimated. However, since all samples were measured under the same conditions, the trends in the relative share of the elements in the samples should be comparable. Small amounts of Mg, Si, P, S, and Ca were present in all samples (in total less than 1 wt.%) and are assumed to be originated from the initial tea leaves that were used as carbon source.

TEM micrographs were recorded to investigate the morphology, size, and distribution of the Co-based nanoparticles on the activated carbon. As seen in Figure 2, all micrographs show that the Co-based nanoparticles are unevenly distributed over the support material. The high-resolution images reveal that the rather large Co-based particles are agglomerates of smaller crystallites. The average sizes of these crystallites are in good agreement with the crystallite size calculated with the Scherrer equation. For the H₂-Co sample, for which the crystallite size of Co could not be determined with the Scherrer method, the average Co particle size is determined to be 14 nm from 30 different particles. Thus, the particles have a comparable size as those of the other samples. Additionally, the STEM-EDX image in Figure S1 shows the formation of an oxygen-containing shell around the Co core. This proves successful surface passivation of the Co nanoparticles with an oxide layer to prevent total oxidation of the metallic species. It further supports the observation in the XRD pattern, where a small amount of CoO was also observed in the H₂-Co sample. Further, the activated carbon material looks similar for all the samples showing amorphous carbon with no specific structure as was already observed from the hump of amorphous carbon in the XRD patterns. It appears that the developed synthesis method is suitable to produce transition metal-based nanoparticles supported on activated carbon and their crystal structures as well as oxidation states can be selectively tuned by using a proper post-treatment method. The nanoparticles and the carbon structure are stable under oxidative and reductive treatments.

To gain more insights into the morphology of the activated carbon material and the distribution of the Co-based nanoparticles and their elemental composition, HR-SEM measurements were coupled with an elemental mapping and the results are presented in Figure S2. For the as-made-CoO sample, the oxygen is mainly located at the Co-based nanoparticles, meaning that relatively more oxygen is bound in CoO, and Co(OH), than on the carbon support. The same trend in oxygen distribution can be seen in the EtOH-CoO sample. Thus, a reducing atmosphere of ethanol vapor predominantly removes oxygen from the carbon support, leaving most of the oxygen associated with the Co-based nanoparticles. For the H₂O₂-CoO₂ sample, the oxygen in the material is rather associated with the carbon material than with the Co. This indicates that the relatively mild oxidation of the sample from decomposing H₂O₂ into *OH and *OOH radicals leads to a high amount of oxygen functionalization of the carbon material. Thus, it hints at a higher amount of oxygen in the carbon material for the H₂O₂-CoO₂ sample than for the as-made-CoO sample.

This fits to the previous finding from the bulk EDX analysis that the H₂O₂-CoO₂ sample contains the highest amount of oxygen compared to the other materials. For the sample reduced under H₂ atmosphere, it is not surprising that almost no oxygen can be found at the Co locations because the Co nanoparticles are mainly in a metallic state. There is only a small surface layer of CoO from the passivation step during the synthesis, which is supported by the small CoO humps in the XRD pattern and the STEM-EDX images of this sample. Consequently, most of the oxygen of the sample is distributed over the carbon material. The presence and distribution of oxygen in the four samples relative to carbon and Co is expected considering the respective treatments during the synthesis.

The textural properties of the materials were further analyzed by N₂ physisorption measurements (Figure S3, Table 1, and Table S2). The activation of carbon with KOH yields a high apparent specific surface area of 758 m²·g⁻¹ and a high micropore volume of 0.26 cm³·g⁻¹ for the as-made-CoO sample. After the H₂O₂ treatment, the apparent specific surface area and the
micropore volume decrease to 595 m$^2$ g$^{-1}$ and 0.21 cm$^3$ g$^{-1}$, respectively. It is assumed that the introduced oxygen functional groups on the surface of the carbon material block some of the micropores making them inaccessible for the N$_2$ molecules, thus resulting in a lower apparent specific surface area and lower micropore volume.\textsuperscript{30} The presence of additional oxygen functional groups is already indicated by the amount of oxygen in the H$_2$O$_2$-Co$_3$O$_4$ sample from the bulk EDX and HR-SEM analysis. The values for the apparent specific surface area and micropore volume for the samples EtOH-CoO (929 m$^2$ g$^{-1}$ and 0.33 cm$^3$ g$^{-1}$) and H$_2$-Co (1065 m$^2$ g$^{-1}$ and 0.38 cm$^3$ g$^{-1}$) fit nicely to this assumption. The reductive treatments of these two samples remove some of the oxygen functional groups making more micropores accessible for the N$_2$. Further, the thermal treatment at 270 °C (EtOH-CoO) and 350 °C (H$_2$-Co) may cause some degree of carbon decomposition where gaseous carbon compounds are released that leave additional micropores behind. For all samples, the mesopore volume is very similar (0.13–0.15 cm$^3$ g$^{-1}$) indicating that the different post-treatments of the as-made-CoO sample do not significantly affect the mesoporosity of the carbon material. Thus, the activation of the carbon from tea leaves with KOH results in a typical, mainly microporous material that supports the Co-based nanoparticles. The developments of micropore volume and apparent specific surface area agree with the oxygen content in the material and can be ascribed to different amounts of oxygen functional groups blocking the micropores.

Further, XPS measurements were conducted to analyze the surface composition and oxidation state of the materials and the spectra are depicted in Figure 3. By looking at the C 1s region (Figure 3a), the ratio of C=–C, C=O single bonds, and C=O double bonds can be evaluated.\textsuperscript{54} For the investigated samples, the deconvolution of the spectra is challenging due to the low resolution of the respective species. Thus, a quantitative analysis of the several species and a comparison of binding energies is not reliable. However, the H$_2$O$_2$-Co$_3$O$_4$ sample displays the highest shoulder in the C=O double bonds region (~288.2 eV) compared to all other samples indicating a highly oxidized carbon material. This is in good agreement with the results of EDX analysis and N$_2$ physisorption that already indicated a higher degree of oxygen functionalization compared to the other samples. Following, the as-made-CoO, and the EtOH-CoO samples show a slightly higher intensity around 286.7 eV compared to the H$_2$O$_2$-Co$_3$O$_4$ sample that hints at relatively more C=O functional groups than C=C=O bonds in these two materials. This is expected because the as-made-CoO, and the EtOH-CoO samples should be less oxidized than the H$_2$O$_2$-Co$_3$O$_4$ sample. For the H$_2$-Co sample, the intensity of the C–O and C=O region is the lowest compared to the C=C=O signal among all measured materials. This result fits well to the findings of the previous analysis techniques that show the highest degree of reduction of the carbon material. The oxidation state of the Co-based nanoparticles on the surface can be determined by looking at the Co 2p$_{3/2}$ satellites in the Co 2p region (Figure 3b). A high shoulder at the binding energy of 786.5 eV is characteristic for Co$^{3+}$ ions whereas a smaller shoulder that stretches to 789.5 eV is caused by Co$^{2+}$ ions.\textsuperscript{55} In agreement with the XRD patterns, the as-made-CoO sample and H$_2$O$_2$-Co$_3$O$_4$ samples both display a stronger Co$^{3+}$ satellite compared to the EtOH-CoO and H$_2$-Co samples. This is caused by Co$^{3+}$ ions of the Co$_3$O$_4$ spinel phase. Additionally, the shoulder at 786.5 eV is a bit higher for the as-made-CoO sample than for the H$_2$O$_2$-Co$_3$O$_4$ sample, which can be explained by the presence of more Co$^{3+}$ ions related to the Co(OH)$_2$ phases. The EtOH-CoO sample has the most pronounced shoulder at 786.5 eV among all samples indicating that this sample has the highest amount of Co$^{3+}$ ions on the surface due to the CoO rock salt structure. For the H$_2$-Co sample, no signal for metallic Co could be found, but a high intensity of the Co$^{2+}$ satellite is observed. Since XPS is a surface-sensitive technique, it only detects the CoO from the passivation of the metallic Co nanoparticles under an atmosphere of 1% O$_2$ in Ar to prevent uncontrolled oxidation of the nanoparticles.

![Graph](image_url)
This passivation layer of CoO is observed in the XRD pattern as well as in the STEM-EDX mapping of the H$_2$–Co sample. Consequently, the general trends of the oxidation state of the Co-based nanoparticle surface follow the trends of the crystal phase from the XRD patterns. However, it should be pointed out that no sample purely contains Co$^{2+}$ ions or Co$^{3+}$ ions on its surface but rather a mixture of both, where the ratio between Co$^{2+}$ and Co$^{3+}$ changes depending on the treatment of the samples.

To investigate how nitrogen was incorporated into the activated carbon material, the XPS spectra of the N 1s region were further analyzed (Figure S4). All samples contain a higher amount of pyrrolic N-species (∼400.4 eV) than pyridinic N-species (∼398.4 eV) that originate from both, the tea leaves and the urea added during the synthesis. Since all samples display similar spectra in the N 1s region it is assumed that the influence of nitrogen on the electrocatalytic properties is similar for all samples. Thus, although improving the overall electrochemical properties of the carbon materials, the nitrogen incorporation should not affect the comparability of the samples.

At last, Raman spectroscopy was used to investigate the spatial distribution of Co-based nanoparticles over 300 μm$^2$ and the degree of graphitization of the activated carbon support (Figure S5). All bands associated with Co are those of CoO$_2$ (684, 617, 520, 479, and 190 cm$^{-1}$). No band could be assigned to CoO or Co(OH)$_2$, which indicates that all Co-based nanoparticles were completely oxidized under the irradiation of the laser. Although the crystal phase of the Co-based nanoparticles was changed, the spatial distribution of the particles can be still estimated from these scans. For the as-made-CoO$_x$, H$_2$O$_2$-CoO$_x$, and H$_2$-Co samples, the intensities of the CoO$_2$ bands vary a lot between the spectra hinting at an uneven distribution of domains with high and low CoO$_2$ contents. It is somehow expected that there would be preferred domains for the location of Co$^{2+}$ ions during the impregnation procedure. Assumingly, during the impregnation of the tea leaves, the Co$^{2+}$ ions diffuse preferably in the porous transportation network of the tea leaves structure leading to a heterogeneous distribution of Co-based agglomerates. In contrast, the sample treated under ethanol vapor atmosphere shows similar intensities for the CoO$_2$ bands in all spectra indicating a homogeneous distribution of Co throughout the carbon material. This result supports the assumption made from the XRD analysis that CoO particles spread under ethanol treatment and disperse over the carbon material.

Although there is no sufficient long-range order in the carbon material judging from the broad hump between 20–30° 2θ in the XRD pattern, there can still be domains in the carbon material that have graphitic characteristics but are rather bent than stacked in parallel layers. In this case, Raman spectroscopy gives hints on defect and graphitic structures in the carbon material. The D-band around 1325 cm$^{-1}$ is caused by defect and disordered structures, e.g., functional groups on the carbon surface. In contrast, the G-band around 1589 cm$^{-1}$ originates from extended aromatic sp$^2$-hybridized structures from the graphitic domains in the carbon material. Thus, the ratio of the intensities of the D-band and the G-band ($I_D/I_G$) can be interpreted as the proportion of defect and graphitic structures in the carbon material. Higher shares of graphitic domains in the carbon material are associated with a better electrical conductivity due to an expanded π-electron system. In contrast, high amounts of defect structures disturb the conjugated π-electron system due to the localization of the electrons at the defect sites. With that in mind, it is not surprising that the H$_2$O$_2$-CoO$_x$ sample, which contains the highest amount of oxygen functional groups as shown by EDX and XPS, also displays the highest $I_D/I_G$ ratio of 5.9. The $I_D/I_G$ ratio of the other samples follows the trend of the degree of reduction, where the as-made-CoO$_x$ sample has an $I_D/I_G$ ratio of 5.4, the EtOH-CoO and H$_2$-Co samples ratios of 5.1 and 4.7, respectively. Thus, a lower $I_D/I_G$ ratio indicates a lower amount of oxygen functional groups in the carbon materials. Therefore, the materials have a higher proportion of graphitic structures with higher electrical conductivity.

The detailed characterization of these materials confirmed that the approach to use tea leaves as a template and carbon source for the synthesis of Co-based nanoparticles leads to a diverse class of Co-based catalysts supported on activated carbon with a variety of different properties. Thus, for the as-made-CoO$_x$ sample as starting point, the impregnation with Co(NO$_3$)$_2$·6 H$_2$O and KOH leads to the formation of Co(OH)$_2$ and Co$_3$O$_4$ nanoparticles supported on activated carbon. The further treatment with H$_2$O$_2$ leads to total oxidation of the Co-based particles to CoO$_2$ and introduced further oxygen functional groups to the carbon support. With reductive treatments under ethanol vapor and H$_2$ gas flow, the oxygen was gradually removed from the material. This results in fewer defect sites in the carbon structure and the formation of CoO and metallic Co nanoparticles, respectively. Remarkably, under ethanol vapor treatment the Co-based nanoparticles tend to spread over the activated carbon support to form small crystallites with an average size of around 6 nm. These Co-based nanoparticles supported on activated carbon with tunable physicochemical and structural properties can be functional catalysts for diverse catalytic reactions. As proof of the concept, the influence of the different post-treatments on the catalytic performance of the materials is studied for the electrochemical OER.

Figure 4 recaps the results of the electrocatalytic experiments including linear sweep voltammograms (LSVs), cyclic voltammograms (CVs), and mass activities of the samples as well as of the ordered mesoporous Co$_3$O$_4$ reference. As seen in Figure 4a, the compositions of the electrocatalysts have a significant influence on the delivered current densities. Among those materials, the EtOH-CoO and as-made-CoO$_x$ samples delivered the highest and the lowest current densities of 141 and 42 mA cm$^{-2}$ at 1.7 V, respectively (solid lines). Despite the lower number of active cobalt species, EtOH-CoO delivers a much higher current density in comparison to the pristine mesoporous Co$_3$O$_4$ reference sample. Further, all carbon-supported samples go through an alteration and lose their initial activities after 50 CVs measurements (Figure 4a). The drop of current densities significantly depends on the oxidation state.
and crystal structure of the cobalt, which will be elaborated below in detail.

The LSVs after the 50 CVs (Figure 4a, dashed lines) show that the as-made CoO and H₂O₂-CoO₃ samples have similar catalytic performances by showing current densities of 33 and 30 mA cm⁻² at 1.7 V and requiring overpotentials of 407 and 406 mV to reach 10 mA cm⁻², respectively (Table 1). In contrast, the EtOH-CoO and H₂-Co samples outperformed the as-made CoO and H₂O₂-CoO₃ samples with current densities of 65 and 66 mA cm⁻² at 1.7 V and overpotentials of 380 and 377 mV at 10 mA cm⁻², respectively. After 50 CVs, the mesoporous CoO₃ reference sample does not display a substantial drop of current density. It has the highest current density of 108 mA cm⁻² at 1.7 V and needs an intermediate overpotential of 397 mV to reach 10 mA cm⁻².

The drop of current density for the activated carbon-supported materials after 50 CVs is stronger compared to the unsupported mesoporous CoO₃. This gives a hint that the drop of current density is not necessarily related to the Co species, but it rather might be attributed to alteration of the carbon materials or the carbon-cobalt interaction. To investigate the reason for this, the EtOH-CoO sample was further studied in detail because it has the most severe drop of current density. For that, the EtOH-CoO sample was loaded on carbon paper and used as a working electrode that can be more feasibly characterized. The alteration of the material was first investigated by SEM analysis and elemental mapping before and after the 50 CVs of the OER measurement (Figure S6). The density and distribution of the nanoparticles over the carbon paper decreased dramatically, which indicates particle detachment during the electrochemical measurements. Further, the elemental mappings from Co and F (which originates from the Nafion) show a decrease in intensity after the OER measurement. This kind of particle detachment from the carbon paper indicates that the interactions between the catalyst particles and the electrode surface are rather weak and small changes in the system (for example applying a potential) may be sufficient to cause particle detachment.

Raman spectra of the EtOH-CoO sample on carbon paper further confirm the detachment of particles during the electrochemical measurement (Figure S7). Although the intensities for the G-band and D-band are much higher due to the carbon paper, the most intense band of CoO₃ at 684 cm⁻¹ is still observable before the OER measurement showing that the catalyst is homogeneously distributed over the carbon paper. After the 50 CVs, the band at 684 cm⁻¹ is only observable at a few spots of the sample meaning that there is a loss of Co on the carbon paper. Further, next to the G-band appears a D'-band at 1615 cm⁻¹ that is characteristic for disordered graphene layers and originates from pure carbon paper. Thus, there is only a small amount of activated carbon support left on the electrode material.

In addition, the EtOH-CoO sample was recovered from the glassy carbon electrode after the 50 CVs of the OER measurement and analyzed by TEM to investigate the CoO nanoparticle distribution as well as the change of the morphology of the material. After the 50 CVs, there is a drastic change in the distribution of Co-based nanoparticles, as seen in Figure S8. In the outer layer of the particles, there is mainly amorphous activated carbon support material and only a few Co-based...
nanoparticles could be observed at the surface of the particle. It can be concluded that the Co-based nanoparticles at the outer layer of the carbon support were leached into the electrolyte during the electrochemical measurements, which caused the significant drop of current density.

To prove that Co leached from the carbon-supported catalysts, the 1 M KOH electrolyte was analyzed after the 50 CVs with ICP-OES to detect dissolved Co species. The results of these measurements were divided by the mass of Co on the electrode for normalization and are presented in Table 2. All activated carbon-supported catalysts independent of the post-treatment leach significantly more Co into the electrolyte (0.5–1.9 ppb μg$^{-1}$Co) than the pristine mesoporous CoO$_x$ (0.1 ppb μg$^{-1}$Co). This could be related to the interaction between the surface of the materials and the Nafion as a binder between the catalyst and the glassy carbon electrode. It is theorized that the sterically demanding hydrophobic Nafion polymer interacts stronger with the mesoporous hydrophobic CoO$_x$ than with the microporous, mainly hydrophobic carbon support particles. Thus, during an experiment, the Nafion can retain more of the mesoporous CoO$_x$ on the electrode than of the activated carbon-supported samples. Therefore, there is less Co as active species left on the electrode for the activated carbon-supported samples than for the mesoporous CoO$_x$ to perform the conversion of OH$^-$ to O$_2$, leading to the observed drop of current density after 50 CVs that is seen in Figure 4a.

Next to the loss of active species from the electrode, the alteration of the surface of the Co-based particles under the oxidizing conditions can influence the OER activity as well. The surfaces of the reduced materials EtOH-CoO and H$_2$-Co are more dominantly affected by the electrochemical measurements as seen from the 1st and 50th CV that are presented in Figure 4b–d. Here, the anodic signal at 1.1 V indicates the oxidation of Co$^{2+}$ to Co$^{3+}$.[61] The EtOH-CoO and the H$_2$-Co samples undergo a strong and irreversible surface alteration under the oxidizing stress as observed from the changing intensities and the shifting potentials of the anodic signal at 1.1 V. The as-made-CoO$_x$ sample (that contains Co(OH)$_2$ and CoO$_x$) also displays a small amount of oxidation at 1.1 V, whereas the H$_2$O$_2$-CoO$_x$ sample and the mesoporous CoO$_x$ material do not change significantly under the oxidizing stress at this applied potential range (Figure S9). At higher potentials, all samples undergo another, yet reversible oxidation step as seen by the anodic peaks around 1.4 V in the CVs (Figure 4). This can be ascribed to the oxidation of the cobalt to the electrocatalytically more active Co$^{3+/4+}$ species. This is consistent with operando X-ray absorption spectroscopy (XAS) studies that verify formation of the active sites for the OER at higher applied potentials. It is well-known that the surface of CoO$_x$ oxidizes into a nonstoichiometric Co$_x$(OH)$_y$ under applied potential.[62] Going along with these observations, it has been proposed that the resting state of the Co species is in the oxidation state 3+ and transitions between the Co$^{3+}$ and Co$^{4+}$ species are the key steps for the catalytic mechanism.[63] In-situ Raman spectroscopy also suggests that under applied potential the population of Co$^{3+}$ species at the surface increases, leading to a more active OER catalyst.[64]

Although the electrocatalytically active Co species are the same for all materials, the structural properties of the initial samples have a crucial impact on the catalytic activity of the materials in terms of the accessibility of active sites, the electrical conductivity as well as the nature of defects.

To confirm the irreversible change of the surface composition of the reduced samples after the 50 CVs of the electrochemical measurement, the EtOH-CoO sample on carbon paper was further analyzed with XPS (Figure S10). Before the OER measurement, the Co 2p region shows a shoulder at 786.7 eV as also seen in Figure 3b that is characteristic for Co$^{3+}$. Due to the loss of particles during the OER measurement, the intensity of the Co 2p signals was significantly lower after the 50 CVs of the OER measurement. However, judging from the disappearance of the shoulder at 786.7 eV and the shape of the Co$^{2+}/3+$ satellite region from 784.5–790.5 eV, the remaining surface Co species seem to be rather in a Co$^{3+}$ state. This finding further supports the previous results from the CV measurements that the reduced Co species undergo a harsh surface alteration under applied oxidizing potential.

Table 2. Concentrations of leached Co in the electrolytes after 50 CVs normalized to the mass of Co on the electrode.

| Sample               | Leached Co normalized to the mass of Co on the electrode [ppb μg$^{-1}$Co] |
|----------------------|-----------------------------------------------------------------------------|
| as-made-CoO$_x$      | 0.9                                                                         |
| H$_2$O$_2$-CoO$_x$   | 1.9                                                                         |
| EtOH-CoO             | 0.5                                                                         |
| H$_2$-Co             | 1.0                                                                         |
| mesoporous CoO$_x$   | 0.1                                                                         |

Although the current densities of the carbon-supported Co-based samples at 1.7 V decrease with ongoing electrochemical treatment, they are stabilized after 50 CVs and still show decent values. To highlight their catalytic performance, the achieved currents of the samples at 1.7 V vs. RHE after 50 CVs were normalized to the mass of Co (Figure 4f, the calculation is shown in the Supporting Information). Here, the EtOH-CoO and H$_2$-Co samples show much higher mass activities of 2.9 and 2.5 A mg$^{-1}$ compared to the as-made-CoO$_x$ and H$_2$O$_2$-CoO$_x$ samples that have mass activities of 1.5 and 1.6 A mg$^{-1}$, respectively. These high mass activities for the reduced samples EtOH-CoO and H$_2$-Co could be partly attributed to the rather conductive carbon supports with lower amounts of oxygen functional groups compared to the carbon supports of the as-made-CoO$_x$ and H$_2$O$_2$-CoO$_x$ samples as it was determined by Raman spectroscopy and XPS.

This is further supported by the Nyquist plots from the electrochemical impedance spectroscopy (EIS) measurements, which give key information about the electrical resistance of the catalysts (Figure S11). The complexity of the catalysts consisting of different materials, dissimilar conductivities, and a complex porous system makes it difficult to model an equivalent circuit of the system. However, the qualitative comparison of the semicircles in the spectra shows the lowest charge transfer resistance for the H$_2$-Co sample, followed by the EtOH-CoO, the as-made-CoO$_x$, and H$_2$O$_2$-CoO$_x$ samples.

This can be concluded that the Co-based nanoparticles at the outer layer of the carbon support were leached into the electrolyte during the electrochemical measurements, which caused the significant drop of current density.
sequently, the trend of electrical resistance of the materials agrees with the conductivity of the samples proposed from the Raman measurements. In addition, for the ETOH-CoO sample, the CoO nanoparticles are much smaller and more evenly distributed over the carbon support compared to the other samples as proven by XRD and Raman spectroscopy, thus exposing a higher surface area of catalytically active material. It is worth mentioning that all four activated carbon-supported samples show a higher mass activity than the mesoporous CoO\textsubscript{2} reference sample (1.2 Amg\textsubscript{Co}/g\textsuperscript{-1}). This indicates the potential of supporting Co\textsubscript{3+} based nanoparticles on a conductive high surface area support material for electrochemical applications.

At last, the long-term stability of the most active sample was investigated by chronopotentiometry. It is usually carried out at current densities of 10 mA cm\textsuperscript{-2}, which means that lower potentials are applied compared to the usual LSV and CV measurements. Under these milder experimental conditions, the ETOH-CoO electrocatalyst shows good stability. As seen in Figure S12, the potential of the sample does not increase to keep 10.2 mA cm\textsuperscript{-2} (which corresponds to a current of 2 mA) over 10 h. In the first 2 h, there is a small variation of the potential, which can be ascribed to an initial activation phase, in which the CoO nanoparticles are slowly oxidized to the electrocatalytically active Co\textsuperscript{3+}/Co\textsuperscript{4+} species.[43] The spikes in the potential profile are attributed to oxygen bubbles that are slowly forming and then rapidly detached from the electrode surface.[43] Accordingly, although the catalyst suffers from a rapid drop of current density at higher applied potentials, the durability of the activated carbon-supported Co-based material is good under milder operating conditions.

**Conclusion**

For the first time this work presents a showcase for a versatile, sustainable, and scalable synthesis approach of Co-based nanoparticles supported on activated carbon by combining tea leaf templating and KOH activation in one step. By choosing the appropriate post-treatment with either H\textsubscript{2}O\textsubscript{2}, ETOH vapor, or H\textsubscript{2} the crystal structure and the oxidation state of the Co species were easily tuned. While the treatment with H\textsubscript{2}O\textsubscript{2} results in CoO\textsubscript{2} nanoparticles supported on a highly functionalized carbon material, the treatment under reducing ethanol atmosphere results in even smaller and homogeneously distributed CoO nanoparticles, whereas the treatment under H\textsubscript{2} gives metallic Co phases. When these materials are used as electrocatalysts for the ORR, the ETOH-CoO sample exhibits the highest activity due to a combination of a relatively conductive activated carbon support and high amounts of accessible catalytic active sites because of the better dispersion of the nanoparticles. All samples outperformed the ordered mesoporous CoO\textsubscript{2} reference material by taking the mass activity of the cobalt species into account. Although the carbon-supported Co-based materials suffer during the electrochemical measurement at higher potential ranges, they show good durability to deliver a current density of 10.2 mA cm\textsuperscript{-2} over 10 h. The presented synthesis protocol extends the toolbox for the universal production of transition metal-based nanoparticles supported on activated carbon that can be used in a wide range of catalytic processes beyond electrocatalytic applications.

**Experimental Section**

**Chemicals.** Co(NO\textsubscript{3})\textsubscript{2}·6 H\textsubscript{2}O (\textgtrsim 98 %), urea (\textgtrsim 98 %), 2-propanol (99.5 %), and Nafion 117 solution (~ 5 % in a mixture of lower alcoholic alcohols and water) were purchased from Sigma Aldrich, KOH (86%) was supplied from VWR and H\textsubscript{2}O\textsubscript{2} (35 % in water) and HCl (37 %) from J. T. Baker. The carbon paper (Toray Carbon Paper, TGP-H-60, PTFE treated) was purchased from Alfa Aesar.

The ethanol had technical grade. The above-mentioned chemicals were used without further purification. Before use, tea leaves (Meylana Goran Tea) were repeatedly washed with hot distilled water (roughly 2 l per 100 g tea leaves) until the washing water had a faint yellow color. Afterwards, the tea leaves were dried at 60 °C overnight and ground to a powder.

**Impregnation of tea leaves.** To impregnate the tea leaves with Co\textsuperscript{2+} ions, 4 g of tea leaves and 2 g of Co(NO\textsubscript{3})\textsubscript{2}·6 H\textsubscript{2}O were mixed in a round-bottom flask. After the addition of 30 mL distilled H\textsubscript{2}O, the suspension was stirred for 2 h at room temperature. Subsequently, the impregnated tea leaves were dried at 60 °C for 2 days.

**Nitrogen incorporation and KOH activation.** To further increase the amount of nitrogen in the carbon material originating from the tea leaves, 250 mg urea was mixed with the impregnated tea leaves in a 250 mL beaker. In a second beaker, 4 g KOH was dissolved in 20 mL H\textsubscript{2}O (tea leaves/KOH weight ratio of 1). The KOH solution was added to the tea leaves/urea mixture and shaken until all of the tea leaves material was wetted from the KOH solution. The resulting slurry was dried overnight at 110 °C and then ground to a powder. Pyrolysis was done at 600 °C (5 K min\textsuperscript{-1}) for 5 h under flowing Ar atmosphere (200 mL min\textsuperscript{-1}). Before the activated sample was exposed to the atmosphere, the material was passivated in a gas flow of 100 mL min\textsuperscript{-1} 1 % O\textsubscript{2} in Ar for 1 h at room temperature to prevent uncontrolled oxidation of the reduced Co nanoparticles.

**Washing of the CoO\textsubscript{2}@activated carbon material.** To remove residual K-containing salts from the material, it was washed thoroughly with water. First, 2.5 g of the sample was dispersed in 40 mL of distilled H\textsubscript{2}O and sonicated for 40 minutes. Afterwards, the CoO\textsubscript{2}/activated carbon material was filtrated and washed further with 2 liters of hot water (~ 70 °C) until the filtrate was pH neutral. The material was dried at 110 °C overnight and is further denoted as "as-made-CoO\textsubscript{2}".

**Oxidation of the as-made-CoO\textsubscript{2} sample.** For oxidation, 500 mg of the as-made-CoO\textsubscript{2} sample was placed in a 500 mL round-bottom flask. Over a dripping funnel, 300 mL of concentrated H\textsubscript{2}O\textsubscript{2} solution was slowly added to the carbon material under constant stirring over several hours to reduce a sudden gas and heat formation. The oxidized material was filtrated and dried at 110 °C overnight. This sample is denoted as "H\textsubscript{2}O\textsubscript{2}-coated-CoO\textsubscript{2}".

**Partial reduction of the as-made-CoO\textsubscript{2} sample.** To reduce the Co-based particles selectively to Co\textsubscript{0}, a mild reduction under ethanol vapor atmosphere was chosen.[44] The as-made-CoO\textsubscript{2} sample was placed inside a tube furnace and an Ar flow rate of 100 mL min\textsuperscript{-1} was applied. Before entering the furnace, the Ar was passed through a bubbler filled with pure ethanol at room temperature to saturate the Ar with the alcohol. The sample was heated with...
briefly, 3.7 mL of a 0.8 M Co(NO$_3$)$_2$·6 H$_2$O solution in ethanol was added to 500 mg of Kit-6 and stirred for 1 h before drying at 50 °C. The ground powder was calcined at 200 °C for 4 h to decompose the Co precursor into CoO. The impregnation step was repeated with 2.3 mL of the same Co precursor solution with subsequent drying and calcination. After the second temperature treatment at 200 °C, the material was heated up to 500 °C for 6 h to obtain highly crystalline Co$_3$O$_4$. To remove the Kit-6 hard-template, the sample was treated with 2 M NaOH at 90 °C overnight. Afterwards, the ordered mesoporous Co$_3$O$_4$ was thoroughly washed with water and dried at 50 °C. The characterization and physicochemical properties of ordered mesoporous Co$_3$O$_4$ are described in a previous publication.$^{[6] (3)}$ This sample is used as reference material for OER and is denoted as ‘mesoporous Co$_3$O$_4$’.

Characterization. Powder X-ray diffraction (XRD) patterns were collected with a Stoe theta/theta diffractometer in Bragg-Brentano geometry using Cu Kα$_1$ radiation (1.5406 Å). A Si PIN diode point detector from Stoe was used as the detector that filters the fluorescence radiation of Co. Transmission electron microscopy (TEM) was performed with a Hitachi HF-2000 electron microscope applying an acceleration voltage of 200 kV. Scanning transmission electron microscopy coupled with energy dispersive X-ray spectroscopy (STEM-EDX) was performed with a Thermo Scientific Talos F200X instrument. It was operated at 200 kV acceleration voltage and is equipped with a SuperX EDX system comprising four silicon drift detectors. High-resolution scanning electron microscopy (HR-SEM) with elemental mapping was conducted with an S-5500 scanning electron microscope from Hitachi with an acceleration voltage of 30 kV. An UltraDry X-ray detector from Thermo Fisher Scientific was used as the detector for EDX in combination with the SEM. N$_2$ physisorption was performed with a 3Flex device from Micromeritics at 77 K. Before every measurement, the samples were activated for 10 h at 350 °C under vacuum. The apparent specific surface area was determined with the Brunauer-Emmett-Teller (BET) method applied for the relative pressure range from 0.02 to 0.07. It should be mentioned that this method is strictly not applicable to calculate the specific surface area of microporous materials and the obtained values do not represent absolute surface areas. However, by analyzing the same range in partial pressure for all samples, the obtained numbers for the apparent specific surface areas are comparable.$^{[24]}$ Further, the micro- and mesopore volume was determined by applying the non-local density functional theory (NLDFT) model for slit pores on a carbon surface at 77 K. X-ray photoelectron spectroscopy (XPS) measurements were performed with a customized spectrometer from SPECS using a hemispherical analyzer (PHOBOS 150 TD Double-Delayline Detector). The monochromatized Al Kα X-ray source (£=1486.6 eV) was operated at 15 kV and 13.3 mA for a total power of 200 W. An analyzer pass energy of 50 eV and 20 eV was applied for the survey scans and the high-resolution scans, respectively. The medium area mode was used as lens mode. The base pressure during the experiment in the analysis chamber was between 2·5·10$^{-10}$ mbar. To account for charging effects, all spectra have been referred to the C 1s signal at 284.5 eV. Raman spectra were recorded with a Renishaw inVia Raman spectroscopy. The laser (785 nm, 15 mW) was focused on the sample surface with a 50 χ magnifying objective. In each scan, 18 different spots were irradiated to measure electro-De. A grating of 1200 mm$^{-1}$ and a CCD array detector (1024×256 pixels) were used to achieve a spectral resolution of 1–2 cm$^{-1}$. For the analysis of the D-band (~1325 cm$^{-1}$) and G-band (~1589 cm$^{-1}$), all spectra were deconvoluted using the Bruker Topas 6 software by using pseudo-Voigt profile functions. The integrals of the deconvoluted bands were used to determine the I$_D$/I$_G$ ratio (an exemplary deconvolution is shown in Figure S13). The SEM micrographs of the as-synthesized paper, as well as the bulk elemental analysis of all samples, were recorded with a Hitachi S-3500N electron microscope equipped with a Si(Li) Pentafet Plus-Detector from Oxford Instruments for elemental mapping. For the determination of the elemental composition of the materials with EDX, five iterations of the sample were taken and the error for all samples was below 0.4 wt.%. The Co-content of the electrolyte was measured with inductively coupled plasma optical emission spectrometry (ICP-OES) with a SPECTROGREEN spectrometer from Spectro Analytical.

Electrocatalytic measurement. To test the electrochemical behavior of the synthesized materials, a three-electrode set-up was used with a glassy carbon rotating disk electrode (AFET3050GC, PINE Research) as working electrode (radius of 2.5 mm, geometric area of 0.196 cm$^2$), a reference hydrogen electrode (RHE, HydroFlex, Gaskatel), and a platinum wire as the counter electrode. The potential was controlled by an SP-150 potentiostat from Biologic. As the electrolyte, 210 mL of a 1 M KOH solution was filled in the PTFE cell and purged with Ar for at least 30 minutes before each experiment to remove dissolved oxygen. During the measurement, the cell was kept under Ar atmosphere and the temperature of the cell was kept constant at 25 °C with a water circulation system. To clean the glassy carbon electrodes, they were polished over cloths with Al$_2$O$_3$ suspensions (MicroPolish Alumina 1 μm and 0.05 μm, Buehler), then sonicated for one minute in water to remove residual Al$_2$O$_3$ and finally dried under an argon flow. For the ink suspension, 4.8 mg of the sample was mixed with 750 μL H$_2$O, 250 μL 2-propanol, and 25 μL Nafion solution. For proper dispersion, the ink suspension was sonicated for 1 h. Afterwards, 5.25 μL of the ink suspension (represents a loading of 0.125 mg cm$^{-2}$) was drop cast onto the cleaned glassy carbon electrode and dried at room temperature under flowing Ar. For the electrochemical measurements, the electrode was rotated at 2000 rpm and scanned with 6 LSVs in the range from 0.7 to 1.7 V vs. RHE with a scan rate of 10 mV s$^{-1}$. Thereafter, 50 CVs were conducted in the range from 0.7 to 1.6 V vs. RHE with a scan rate of 50 mV s$^{-1}$. After the 50 CVs, another three LSVs were recorded with the same scan range and scan rate as the previous LSVs. For the evaluation of the stability of the materials during the electrochemical measurements, the LSVs before and after the 50 CVs were compared. Electrochemical impedance spectroscopy (EIS) measurements were conducted with the same set-up and the same electrode preparation under an applied potential of 1.65 V vs. RHE. The frequency of the alternating current was altered from 10$^2$ to 10$^6$ Hz with an amplitude of 5 mV. The IR drop was compensated at 85 % for all measurements and the reproducibility of the results was proven by measuring three electrodes per sample. For characterization of the samples after the OER in SEM-EDX, XPS, and Raman spectroscopy, 100 μl of the ink was drop cast onto carbon paper (1.5×1.5 cm) and treated under the same electrochemical conditions (6 LSVs, 50 CVs, 3 LSVs). The particles for TEM measurements after OER were recovered from the glassy carbon electrode after the activity test by sonicating the electrode in ethanol. The ethanol/particle suspension was then drop cast onto a TEM grid with a lacey carbon. For the determination of the amount of Co leached into the electrolyte...
with ICP-OES, the electrolyte of each sample was collected and acidified with 10 ml HCl. To increase the concentration of Co ions, roughly 60% water was evaporated at 115 °C. For the stability test, a chronopotentiometric measurement was conducted at a constant current density of 10.2 mA cm⁻² in 1 M KOH electrolyte with 2000 rpm without any previous LSV and CV scans.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: cobalt-based nanoparticles · oxygen evolution reaction · sustainable carbon support · tea leaf templating

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