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Exceptionally Stable And Super-Efficient Electrocatalysts Derived From Semiconducting Metal Phosphonate Frameworks

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Two new isostructural semiconducting metal-phosphonate frameworks are reported. $Co_2[1,4-NDPA]$ and $Zn_2[1,4-NDPA]$ (1,4-NDPA⁴⁻ is 1,4-naphthalenediphosphonate) have optical bandgaps of 1.7 eV and 2.5 eV, respectively. The electrocatalyst derived from $Co_2[1,4-NPDA]$ as a precatalyst generated a low overpotential of 374 mV in the oxygen evolution reaction (OER) with a Tafel slope of 43 mV dec⁻¹ at a current density of 10 mA cm⁻² in alkaline electrolyte (1 molL⁻¹ KOH), which is

Introduction

During the last two decades, metal organic frameworks (MOFs) have been one of the most active research areas.^[1,2] MOFs provide rich structural diversity and reticular chemistry to optimize pore sizes and surface areas in porous materials.^[3-6] Furthermore, MOF surface areas can be decorated with a large variety of organic functional groups via linker design as well as post-synthetic modifications.^[7-11] The rich structural diversity of MOFs has been well reflected in their potential application areas such as small molecule capture,^[12-14] small molecule storage,^[15] electrode materials,^[16,17] electrochemical energy storage,^[18] magnetism,^[19,20] drug delivery,^[21-23] heterogeneous catalysis of the oxygen evolution reaction (OER) is one of the fundamental steps in electrochemical systems such as water splitting or zinc-air batteries.^[29-31] Design and synthesis of novel

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indicative of remarkably superior reaction kinetics. Benchmarking of the OER of Co₂[1,4-NPDA] material as a precatalyst coupled with nickel foam (NF) showed exceptional long-term stability at a current density of 50 mA cm⁻² for water splitting compared to the state-of-the-art Pt/C/RuO₂@NF after 30 h in 1 molL⁻¹ KOH. In order to further understand the OER mechanism, the transformation of Co₂[1,4-NPDA] into its electrocatalytically active species was investigated.

OER electrocatalysts with fast kinetics, excellent catalytic activity and stability has been extensively studied during the last years. Metal-based oxides such as IrO2 and RuO2 are the current bench-mark materials for OER due to their low overpotential and large current density.^[32] However, high cost, poor durability, and low earth reserves of IrO2 and RuO2 hinder the feasibility of these compounds for industrial applications.^[33] As an alternative to IrO₂ and RuO₂, MOFs are recently emerging as precatalysts for electrocatalysis of the hydrogen evolution (HER), oxygen evolution (OER), and oxygen reduction reactions (ORR).[34-37] Such compounds could potentially provide more feasible and environmentally friendlier options towards industrialization of OERs.^[38] In the current state of the art, MOFs generally function as precatalysts, undergoing a sequence of structural reconfigurations, such as hydrolysis, metal ion leaching, and oxidation of the metal ions in the alkaline medium to generate an active catalyst such as $[M(OH)_2-M(O)_x(OH)_y]$.^[39]

One of the unexplored material types in electrocatalysis is the use of recently emerging semiconducting metal-phosphonate frameworks. Hypothetically, the use of narrow band gap or semiconducting MOFs might help improve OER kinetics, and currently there is a limited number of narrow band gap MOFs in the literature.^[40] Our research group has recently reported on the electrical conductivity of microporous phosphonate MOFs and layered metal phosphonates.^[17,20,41-44] The reported semiconducting phosphonate MOFs by our group have narrow band gaps between 1.4 and 2.5 eV. We have previously shown that changing the identity and coordination environment of the metal ions in isostructural MOFs and hydrogen-bonded organic framework (HOFs) are important tools for fine band-gap tuning of the framework.^[43,45] The band gap of a compound might be an indicator for the ease of an electron transfer step in electrocatalytic reactions.^[46,47] For example, the Co³⁺/Co²⁺ couple is currently intensely investigated for photocatalytic water splitting because the respective reduction potential at $pH\!=\!7$ is $E^0\!\!\sim\!+1.41$ V >+1.23 V for the OER of pure water. $^{[48]}$ Furthermore, phosphonate-MOFs could exhibit exceptional thermal stabilities above 400 $^\circ\text{C}$ and chemical stabilities between $pH\!=\!0$ and $12.^{[49-54]}$

In this work, we successfully synthesized two new dense isostructural semiconducting metal phosphonate frameworks namely Co₂[1,4-NDPA] and Zn₂[1,4-NDPA] (where 1,4-NDPA⁴⁻ is 1,4-naphthalenediphosphonate) by hydrothermal methods in pure water. The structures were characterized by single crystal X-ray diffraction (XRD), powder-XRD, infrared (IR) and scanning electron microscopy (SEM) with energy dispersive X-ray analysis (EDX). Optical measurements were carried out to determine the absorption onset of the materials. The Co₂[1,4-NDPA] and Zn₂[1,4-NDPA] materials were used for OER on a glassy carbon electrode. Furthermore, the materials were used as cathode and anode on nickel foam (NF) and compared with commercial platinum on carbon (Pt/C) (cathode catalyst) and RuO₂ (anode catalyst) couple for water splitting. The formation of the active species derived from Co₂[1,4-NPDA] was investigated to understand the OER mechanism.

Results and Discussion

Synthesis

Chemicals were purchased from Aldrich, Alfa Aesar and TCI chemicals, and used without further purification. 1,4-naphthalenediphosphonic acid, 1,4-NDPAH₄ was synthesized according to the literature.^[17,55] A detailed description of the linker synthesis can be found in the Supporting Information. Co₂[1,4-NDPA] and Zn₂[1,4-NDPA] were synthesized under the same hydrothermal reaction conditions. Co(NO₃)₂·6H₂O (273 mg, 0.93 mmol) or Zn(NO₃)₂·6H₂O (276 mg, 0.93 mmol), 1,4-naphthalenediphos-phonic acid (100 mg, 0.34 mmol) and 4,4'-bipyridine as a modulator (40 mg, 0.25 mmol) and 10 mL of ultrapure water were placed in a Parr Teflon-lined autoclave. After brief mixing of the reaction mixture, the autoclave was closed and heated to 200 °C for 72 hours. Afterwards, the product was washed three times with 10 mL of ultrapure water and one time with 10 mL acetone prior to drying. The product was dried in air at room temperature, yielding dark blue crystal plates of $Co_2[1,4-NDPA]$ and white crystal plates of $Zn_2[1,4-NDPA]$.

Crystal structure description

The structures of Co₂[1,4-NDPA] and Zn₂[1,4-NDPA] were determined and refined using single crystal X-ray diffraction methods. As depicted in Figure 1a, the two isostructural compounds Co₂[1,4-NDPA] and Zn₂[1,4-NDPA] exhibit a pillared layered metal phosphonate network. The layered secondary building unit (SBU) is constructed from tetrahedrally coordinated Co^{2+} or Zn^{2+} atoms and phosphonate groups ($-PO_3^{2-}$) from the fully deprotonated 1,4-NDPA⁴⁻ linkers, forming isolated four-membered M–O–M–O rings (M=Co or Zn), surrounded by six eight-membered M-O-P-O-M-O-P-O rings to give a layered network of Co₂[1,4-NDPA] and Zn₂[1,4-NDPA] (Figure 1a and 1b). The actual topology of the layered SBU of Co₂[1,4-NDPA] and Zn₂[1,4-NDPA] is unprecedented among other layered metal phosphonate frameworks with a 3,3,4 L25 net type (see Supporting Information for topological characterization). The layered SBUs are connected by aromatic naphthalene units of 1,4-NDPA⁴⁻ to form the three-dimensional framework (see Figure 1a and Supporting Information). The analysis for purity of the single-crystalline phase was done by PXRD. As shown in the PXRD (Figure 2), both Co₂[1,4-NDPA] and Zn₂[1,4-NDPA] show good agreement with simulation and were synthesized as single crystalline phases. As depicted in Figures S1 to S3, the intercentroid distances between the naphthalene moieties for Co₂[1,4-NDPA] and Zn₂[1,4-NDPA] are, respectively, 3.91 Å and 3.97 Å and shortest C---C distances



Figure 1. (a) Section of the packing diagram of the three-dimensional structure of $Co_2[1,4-NDPA]$. (b) Structure of the layered inorganic building unit of $Co_2[1,4-NDPA]$ (isostructural to $Zn_2[1,4-NDPA]$).

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Figure 2. PXRD of the single-crystalline phase in agreement with the simulation from the structure of $Zn_2[1,4-NDPA]$.

3.40–3.48 Å and 3.35–3.44 Å, which are similar to interlayer distances of graphite (for a more detailed description of the crystal structure see Supporting Information).

Optical measurements

Based on the marked color difference of $Co_2[1,4-NDPA]$ and $Zn_2[1,4-NDPA]$, diffuse reflectance spectra were measured on powdered samples of these two compounds in an integrating sphere setup (Ulbricht sphere). If the thickness of the powder slab is sufficiently high such that transmittance along the layer is negligible, the absorbance A of the powder scales with the Kubelka-Munk function K/S given by Equation (1):



with R_{∞} as the diffuse reflectance of the powder layer. The Kubelka-Munk spectra of Co₂[1,4-NDPA] and Zn₂[1,4-NDPA] are depicted in Figure 3. Both spectra show a strong increase around 500 nm (~2.5 eV) and are very similar in that wavelength range. This absorption is assigned to an interband transition, which is expectedly strongly localized at the naphthalene moieties. The low onset energy (< 3 eV) for strong absorption indicates a semiconducting behavior of the two compounds. The strong increase in absorption below 400 nm in the ultraviolet (UV) range of Zn₂[1,4-NDPA] explains why the related powdered compound appears colorless under daylight. The Kubelka-Munk spectrum of Co₂[1,4-NDPA] reveals additional low-energetic broad absorption bands in the range between 500 nm and 700 nm (onset of ~1.7 eV in the energy domain), which are absent in the Zn analogue and thus have to be identified as localized transitions due to the presence of tetrahedrally coordinated Co(II) in Co₂[1,4-NDPA]. The electronic transitions of the tetrahedrally coordinated 3d⁷ ion Co²⁺ can be in principle interpreted by means of the Tanabe-Sugano diagram of an octahedrally coordinated $d^{10-7} = d^3$ ion. Comparison to other literature-reported examples of Co²⁺-doped purely inorganic oxides such as spinel-type $MAI_2O_4:Co^{2+}$ (M=Zn, Mg), $^{[56,57]}$ willemite-type $^{[58]}$ Zn₂SiO₄: Co²⁺ or wurtzite-type $^{[59]}$ binary compounds MX:Co²⁺ (M = Zn, X = O, S) offering tetrahedrally coordinated sites for Co²⁺ allows the assignment to a ${}^{4}A_{2}({}^{4}F) \rightarrow {}^{4}T_{1}({}^{4}P)$ ligand field transition of the observed absorption bands in that wavelength range (see Figure 3). The dark blue color of Co₂[1,4-NDPA] can be related to both the absorption in the deep red to near infrared range ($\lambda > 650$ nm) on the one hand and the strong reflection of light in the blue range of the



Figure 3. Optical Kubelka-Munk spectra of powdered Co₂[1,4-NDPA] (red) and Zn₂[1,4-NDPA] (dark blue) obtained from diffuse reflectance spectra at room temperature. The localized Co(II)-based ligand field transition is denoted

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visible spectrum. Similar colors are known from the pigment Thénard blue (CoAl₂O₄) with high concentrations of Co²⁺, which crystallizes in a spinel-type structure and in which the Co²⁺ ions also occupy tetrahedrally coordinated sites.

Electrocatalytic performance of the OER

The electrochemical OER is an anodic half-cell reaction and produces O₂ at a theoretical input of 1.23 V (vs. reversible hydrogen electrode (RHE)). We investigated the OER using Co₂[1,4-NDPA] and Zn₂[1,4-NDPA] as precatalysts in a 1 mol L⁻¹ KOH electrolyte (pH = 14) and the obtained results were compared with commercial RuO₂. We used a glassy carbon rotating disk electrode (GC-RDE) with a geometric area of 0.196 cm⁻² at a rotating velocity of 1600 rpm in a standard three-electrode system. The mass loading of electrocatalysts on the GC-RDE was quantified at 0.23 mg cm⁻² (see Supporting Information for details). The polarization curves were generated by the linear sweep voltammogram (LSV) of Co₂[1,4-NDPA] and Zn₂[1,4-NDPA] and are compared to β -Co(OH)₂, a physical mixture of β -Co(OH)₂ and the ligand 1,4-NDPAH₄ and commercial RuO₂ in the same Nafion ink (see Supporting Information about how the ink for the electrode was prepared). The synthesized β -Co(OH)₂ and physical mixture of β -Co(OH)₂ and the ligand 1,4-NDPAH₄ were used as reference catalysts. Figure 4a presents the polarization curves of the samples after 20 cyclic voltammetry (CV) cycles of activation at a scan rate 50 mVs⁻¹, in order to get a stable state of the catalysts on the GC-RDE surface. The overpotentials of the various working electrodes are determined to be 374 mV for Co₂[1,4-NDPA], 380 mV for β -Co(OH)₂, 392 mV for the physical mixture of β -Co(OH)₂ and the ligand 1,4-NDPAH₄, 408 mV for Zn₂[1,4-NDPA] and 318 mV for RuO₂ at the current density of 10 mA cm⁻² (see Figure 4a).

The Tafel plots are usually obtained in a potential range where the current is predominantly controlled by catalysis kinetics (non-mass-transfer restriction).^[60] Therefore, we evaluated electrocatalytic kinetics for the OER of the precatalysts Co₂[1,4-NDPA] and Zn₂[1,4-NDPA] by generating their corresponding Tafel slopes. As seen in Figure 4b, the linear portion of the Tafel plot was fitted using the equation $\eta = a + b \times \log j$, where η and *j* represent the overpotential and the current density, respectively; b is the Tafel slope and a represents the cathodic intercept that is related to the exchange current density.^[60] The smaller Tafel slope often refers to more favorable OER kinetics and a better electrocatalytic activity. The OER is a four-electron transfer reaction with a sequence of steps and intermediates, such as MO, MOOH or physisorbed peroxide species.[60] One of the most accepted OER mechanisms is the Krasil'shchikov's pathway, given in Reactions (1)-(4) with their corresponding Tafel slopes (b).[61-63]

$$M + OH^{-} \Leftrightarrow MOH + e^{-}, b = 120 \text{ mVdec}^{-1}$$
(1)

$$MOH + OH^{-} \leftrightarrows MO^{-} + H_2O, b = 60 \text{ mV} \text{dec}^{-1}$$
(2)



Figure 4. a) OER polarization curves before and after 1000 CVs in 1.0 mol L⁻¹ KOH (pH = 14) b) OER Tafel plots obtained from the OER polarization curves c) corresponding overpotentials (columns) before and after 1000 CVs at 10 mA cm⁻² and Tafel slopes (dark cyan dots). (d) raw data Nyquist plots at 1.6 V vs. RHE (symbol) and fitting to an equivalent model (solid line) from EIS test of Co₂[1,4-NDPA], Zn₂[1,4-NDPA], β -Co(OH)₂, physical mixture of β -Co(OH)₂ and ligand 1,4-NDPAH₄ and RuO₂ and benchmark material RuO₂ on GC-RDE.

$$MO^{-} \rightarrow MO + e^{-}, b = 45 \text{ mV} \text{dec}^{-1}$$
(3)

$$2MO \rightarrow 2 M + O_2, b = 19 \text{ mV dec}^{-1}$$
 (4)

Based on the Krasil'shchikov's pathway, a Tafel slope of b =43 mV dec⁻¹ to the OER involving Co₂[1,4-NDPA] corresponds to reaction (3) as a rate determining step. The Tafel slope of $Zn_2[1,4-NDPA]$ (b=82 mV dec⁻¹) falls in between the values of the reaction (1) and (2). This can be attributed to stronger OH⁻ binding to Zn²⁺ ions that accelerates the rate of electron transfer in Reaction (1) (Figure 4b). As presented in Table S6, the Tafel slope of the electrocatalysts derived from Co₂[1,4-NDPA] and Zn₂[1,4-NDPA] is much lower than RuO₂ (62 mV dec⁻¹), β -Co(OH)₂ (52 mV dec⁻¹, the physical mixture of β -Co(OH)₂ and the ligand 1,4-NDPAH₄ (56 mV dec⁻¹) and other Co-based catalysts in the literature,^[38] which suggest its superior reaction kinetics. In addition, the stability of the electrocatalysts derived from Co₂[1,4-NDPA] and Zn₂[1,4-NDPA] was investigated and compared with the commercial benchmark RuO₂ after 1000 continuous CVs. The electrocatalysts derived from Co₂[1,4-NDPA] and Zn₂[1,4-NDPA] showed stronger durability compared to β -Co(OH)₂, the physical mixture of β -Co(OH)₂ and the ligand 1,4-NDPAH₄, and RuO₂, as they exhibited only minor positive shifts of 2 and 8 mV, respectively. RuO₂, β-Co(OH)₂, and the physical mixture of β -Co(OH)₂ and the ligand 1,4-NDPAH₄ showed an increase of the overpotential by 14, 4 and 6 mV, respectively, at the current density of 10 mA cm⁻² after 1000 CVs (see Figure 4c).

To better understand the OER kinetics, an electrochemical impedance spectroscopy (EIS) measurements were carried out at 1.6 V in a frequency range of 0.1 Hz to 100 kHz in 1 mol L⁻¹ KOH. The semicircles in the high-frequency range of the Nyquist plots are attributed to charge-transfer resistance, which is equivalent for all catalysts. The Nyquist plots of catalysts $Co_2[1,4-NDPA]$, $Zn_2[1,4-NDPA]$, β -Co(OH)₂ and the physical mixture of β -Co(OH)₂ and ligand 1,4-NDPAH₄ and RuO₂ were curve-fitted to the model to evaluate the charge transfer

resistance (R_{ct}) (see Figure 4d). The small R_{ct} value indicates the efficient electron transfer between the active sites of catalysts derived from Co₂[1,4-NDPA] and Zn₂[1,4-NDPA] and the electrolyte ion during OER. Co₂[1,4-NDPA] has the smallest R_{ct} value of 8 Ω , which is obviously smaller than that of β -Co(OH)₂ (10 Ω), the physical mixture of β -Co(OH)₂ and the ligand 1,4-NDPAH₄ (13 Ω), RuO₂ (16 Ω) and Zn₂[1,4-NDPA] (21 Ω).

Overall electrochemical water splitting

The overall water splitting contains two half reactions, which are the hydrogen evolution reaction (HER) and the oxygen evolution reaction (OER). The Co₂[1,4-NDPA] and Zn₂[1,4-NDPA] materials were coated on the surface of NF with a uniform thin layer (see SI for experimental details). Both the anode and cathode was constructed by employing the Co2[1,4-NDPA] or Zn₂[1,4-NDPA] materials in the alkaline electrolyzer with 1 mol L⁻¹ KOH. The integrated commercial platinum on carbon (Pt/C) (cathode catalyst) and RuO₂ (anode catalyst) couple (Pt/ C@NF/RuO2@NF) was also tested for comparison. As expected, the LSV curves in Figure 5a show that the Pt/C@NF/RuO2@NF couple catalysed the water electrolysis with an overpotential of 278 and 340 mV at a current density of 10 and 50 mA cm $^{-1}$, respectively. Therefore, the catalysts derived from Co2[1,4-NDPA]@NF (312 mV) and Zn₂[1,4-NDPA]@NF (371 mV) show a lower overpotential compared to the performance of the glassy carbon electrode. Additionally, the activity of Co₂[1,4-NDPA]@NF is higher than the benchmark RuO2@NF, reaching a practical current density of 200 mA cm⁻² at 1.63 V. The long-term stability plays an important role to evaluate electrocatalysts for practical water electrolysis.

The long-term stabilities of the catalysts derived from $Co_2[1,4-NDPA]$ and $Zn_2[1,4-NDPA]$ and the commercial Pt/C/ RuO_2 couple in 1 mol L⁻¹ KOH was further checked by a chronopotentiometric test applying a constant current density at 50 mA cm⁻² continuously for 30 h. The potential of the catalysts derived from $Co_2[1,4-NDPA]$ @NF and $Zn_2[1,4-NDPA]$ -



Figure 5. (a) Polarization curves and (b) the long-term stabilities in the electrolysis at a current density of $\eta = 50 \text{ mA cm}^{-2}$ by chronopotentiometric measurements of Co₂[1,4-NDPA], Zn₂[1,4-NDPA], Pt/C/RuO₂ on NF for overall water splitting in 1 mol L⁻¹ KOH.

@NF remained nearly unchanged during the whole measurement. In contrast, the commercial benchmark Pt/C/RuO₂@NF couple showed an increasing working potential at the current density of 50 mA cm⁻² over 30 h. Consequently, the electrocatalysts derived from Co₂[1,4-NDPA] and Zn₂[1,4-NDPA] adhered well on the surface of NF after the stability test, as proven by SEM and element mapping (Figure S10 and Figure S11).

Zheng *et al.* point out that the metal-organic-framework based catalysts are precatalysts, and change to active phases during the electrochemical treatment under alkaline condition (1 mol L⁻¹ KOH).^[37] Therefore, we tested the chemical stability of Co₂[1,4-NDPA] by soaking the material in the alkaline electrolyte (1 mol L⁻¹ KOH) for 30 min and 24 h, in order to gain a better understanding of the activation mechanism. The PXRD pattern of Co₂[1,4-NDPA] after 24 h in 1 mol L⁻¹ KOH revealed the presence of cobalt hydroxide species (Figure 6). in the form of α -Co(OH)₂ (ICDD: 74-1057) and β -Co(OH)₂ (ICDD: 30-0443). It was indicated that the active sites in α/β -Co(OH)₂ are responsible for the excellent electrocatalyst performance.^[64-66]

Thermal stability

The thermal stability of the Co₂[1,4-NDPA] and Zn₂[1,4-NDPA] was investigated by thermogravimetric analysis (TGA) measurements under a nitrogen atmosphere. Co₂[1,4-NDPA] and Zn₂[1,4-NDPA] show exceptional thermal stability where the organic components start to decompose at ca. 650 °C with 29.1 % experimental weight loss (theoretical 30.9 %) for Zn₂[1,4-NDPA]. The TGA curve of Co₂[1,4-NDPA] indicates a more gradual weight loss with a sharp mass decrease above 650 °C (see Figure S7).



Figure 6. PXRD patterns of Co₂[1,4-NDPA], after 30 min and 24 h in 1 mol L⁻¹ KOH; reflections from β-Co(OH)₂ (ICDD:30-0443) and α-Co(OH)₂ (ICDD: 74-1057). Conclusions

Herein, we report the hydrothermal synthesis of the two new semiconducting metal-phosphonate frameworks Co₂[1,4-NDPA] and Zn₂[1,4-NDPA], and we have shown that changing the metal ions in isostructural semiconducting metal-phosphonate frameworks can be used to tune band gap and semiconducting properties. Both powdered compounds have absorption onsets at around 500 nm (2.5 eV), derived from photoluminescence optical Kubelka-Munk spectra data, which are strongly localized at the naphthalene moieties. Furthermore, Co₂[1,4-NDPA] shows a second onset at 700 nm (1.7 eV) which has to be identified as ligand-field transitions localized at the Co center with its low energetic ${}^{4}A_{2}({}^{4}F) \rightarrow {}^{4}T_{1}({}^{4}P)$ ligand field transition of tetrahedrally coordinated d⁷-Co(II). We have furthermore used the new semiconducting metal-phosphonate frameworks as precatalysts for the OER reaction. We have shown that both Co₂[1,4-NDPA] and Zn₂[1,4-NDPA] are remarkable precatalysts for the OER reaction in water splitting with overpotentials of 374 mV for Co₂[1,4-NDPA] and 408 mV for Zn₂[1,4-NDPA] for a glassy carbon rotating electrode system and 312 mV and 371 mV on NF at a current density 10 mA cm⁻². The Tafel slope of 43 mV dec⁻¹ in 1 mol L⁻¹ KOH at a current density of 10 mA cm⁻² of the Co₂[1,4-NDPA] precatalyst indicates its superior reaction kinetics compared to the commercial benchmark material RuO₂ or other compound families like metal phosphides and some reported MOFs in the literature. Besides, its good reaction kinetics, electrocatalyst derived from Co2[1,4-NDPA] also shows remarkably improved activity, compared to RuO₂ on NF for water splitting reaching a current density of 200 mA cm⁻² at 1.63 V. This work also demonstrated the exceptionally high stability of the derived active species of $\beta\text{-Co(OH)}_2$ and $\beta\text{-}$ CoOOH catalysts by using Co2[1,4-NDPA] as a precatalyst in 1 mol L⁻¹ KOH for 30 h at a constant current density of 50 mA cm⁻². Several features may contribute to the excellent OER performance of the catalyst derived from Co₂[1,4-NDPA] when compared to the concurrently studied RuO_2 , β -Co(OH)₂ and physically mixed β -Co(OH)₂ with the ligand 1,4-NDPAH₄. For example, the Co₂[1,4-NDPA] precatalyst might hypothetically generate a more uniform distribution of α/β -Co(OH)₂ and 1,4-NDPA-H₄ ligand on the surface of the glassy carbon electrode creating superior OER activities compared to the concurrently studied systems. All these results demonstrate that both materials, but especially the Co₂[1,4-NDPA] are potential candidates for industrial applications as precatalysts for OER in water electrolysis.

Supporting Information

Additional detailed experimental and characterization methods; synthesis progress; crystallography information; FTIR measurement; thermogravimetric analysis; electrochemical measurement; SEM and SEM-EDX before and after electrolysis; OER performance comparison; and topological analysis.

Deposition Numbers 2235305 (for $Co_2[1,4-NDPA]$), 2212088 (for $Zn_2[1,4-NDPA]$) contain the supplementary crystallographic

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Conflict of Interests

The authors declare no competing financial interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords: electrocatalysis · phosphonates · semiconducting materials

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