

Electroactive Prussian Blue Analogues/TiO₂ Nanocomposites Obtained through SILAR Assembly in Mesoporous Nanoarchitectures

Priscila Vensaus⁺,^[a, b, c] Rolando M. Caraballo⁺,^[a, b, c] Emiliano Tritto,^[a, b] Cynthia C. Fernández,^[a, b, e] Paula C. Angelomé,^[d] M. Cecilia Fuertes,^[d] Federico J. Williams,^[a, b] Galo J. A. A. Soler-Illia,^{*[a, c]} and Luis M. Baraldo^{*[a, b]}

The preparation of nanomaterials for energy applications such as intercalation batteries and materials that can act as substrates for water oxidation is a subject of major interest nowadays. In this work, we report the deposition of Prussian blue (PB) and its cobalt analogue (CoPBA) on mesoporous titania thin films (MTTF) using the successive ionic layer adsorption reaction (SILAR) technique under soft conditions. A bifunctional ligand, 1,10-phenanthroline-5,6-dione (**pd**), was used to functionalize the titania surface and promote the growth of PB and CoPBA. The resulting PB@MTTF and CoPBA@MTTF nanocomposites were characterized using several

Introduction

To overcome the challenge of global warming it is imperative to transition from the current energy matrix, built on fossil fuels, to one based on renewable sources.^[1,2] Nonetheless, even if the source is renewable, energy needs to be stored and carried in environment-safe ways.^[3] Therefore, energy conversion and storage requires the development of innovative batteries as well as an efficient production of clean fuels.^[4–7] Among the proposed fuels, molecular hydrogen has attracted attention, given its low molecular weight and high energy content per mass unit.^[8] The fact that it can be obtained from a natural and abundant raw material, such as water, by simple electrolytic methods makes it even more appealing.^[9–12] Thus, the water splitting (WS) electrochemical reaction to obtain molecular techniques and it was determined that PB and CoPBA grow in a controlled and sequential manner, maintaining the mesoporous architecture. Both PB@MTTF and CoPBA@MTTF demonstrated very good electroactive properties, while CoPBA@MTTF exhibited water oxidation capabilities. The flexibility of this PBA@MTTF platform allows the incorporation of any labile transition metal ion or fragment into the structure of the coordination polymer embedded into a mesoporous matrix, opening the door for (photo)electrochemical devices and catalysts.

hydrogen and oxygen has been thoroughly studied,^[13-15] and efforts are being made to develop new low-cost catalysts for this reaction and push their efficiency to make the whole process economically viable.^[16]

Homogeneous catalysts have been studied with good results and the reaction mechanisms are now well understood in some systems, particularly those employing ruthenium and iridium coordination complexes.^[17–20] However, these metals are expensive and have a low natural abundance. On the other hand, heterogeneous catalysis is an attractive approach for implementation on a larger production scale, since the catalyst can be easily removed and replaced if necessary. Furthermore, the use of materials such as oxides, phosphates and oxyhydroxides based in first-row transition metal explores the possibility to obtain cost-effective and environmentally friendly

- [a] P. Vensaus,⁺ Dr. R. M. Caraballo,⁺ Dr. E. Tritto, Dr. C. C. Fernández, Prof. Dr. F. J. Williams, Prof. Dr. G. J. A. A. Soler-Illia, Prof. Dr. L. M. Baraldo Universidad de Buenos Aires Facultad de Ciencias Exactas y Naturales Departamento de Química Inorgánica, Analítica y Química Física Pabellón 2, Ciudad Universitaria, C1428EHA, Buenos Aires (Argentina) E-mail: gsoler-illia@unsam.edu.ar baraldo@qi.fcen.uba.ar
- [b] P. Vensaus,⁺ Dr. R. M. Caraballo,⁺ Dr. E. Tritto, Dr. C. C. Fernández, Prof. Dr. F. J. Williams, Prof. Dr. L. M. Baraldo CONICET – Universidad de Buenos Aires Instituto de Química Física de Materiales, Medio Ambiente y Energía (INQUIMAE) Pabellón 2, Ciudad Universitaria, C1428EHA, Buenos Aires (Argentina)
- [c] P. Vensaus,⁺ Dr. R. M. Caraballo,⁺ Prof. Dr. G. J. A. A. Soler-Illia Instituto de Nanosistemas Universidad Nacional de General San Martín-CONICET Av. 25 de Mayo 1169 (B1650KNA), San Martín (Argentina)
- [d] Dr. P. C. Angelomé, Dr. M. C. Fuertes
 Gerencia Química & Instituto de Nanociencia y Nanotecnología
 Centro Atómico Constituyentes, Comisión Nacional de Energía Atómica,
 CONICET
 Av. General Paz 1499 (B1650KNA), San Martín, Buenos Aires (Argentina)
- [e] Dr. C. C. Fernández Lehrstuhl für Physikalische Chemie II Friedrich-Alexander-Universität Erlangen-Nürnberg
- Egerlandstraße 3, 91058 Erlangen (Germany) [⁺] These authors contributed equally to this work.
- Supporting information for this article is available on the WWW under https://doi.org/10.1002/ejic.202300576

0990682c,

photoelectrodes with improved functionality,^[21] and have been studied for water oxidation.^[22-24] In addition, the combination of a heterogeneous WS catalyst and a photoactive material brings up the possibility of harnessing solar energy to activate WS, opening a potential path towards large-scale solar fuel production.^[25-27]

Coordination polymers (CP) are an attractive option to explore as heterogeneous catalysts. These materials maintain characteristics of coordination chemistry which can be transprocedures synthetic and lated to mechanism rationalization.^[28,29] The use of different ligands or post-synthetic functionalization allows for the acquisition of a wide range of tunable properties. Some of the simplest CP present excellent catalytic activity, while they keep costs low and can be prepared using soft synthetic methods. Prussian blue (PB, Fe₃"[Fe^{III}- $(CN)_{6}_{2} \cdot nH_{2}O)$ and Prussian Blue Analogues (PBA, $M_{3}^{\parallel}[Fe^{\parallel}]$ - $(CN)_6]_2 \cdot nH_2O$ where M is a transition metal), including the ones containing cobalt, zinc and manganese, are some of the most well-known examples.^[30-34] PB and PBA have aroused enormous interest in the last years as electroactive materials due to their open framework structure that leads to high accessibility and reversibility, together with their low cost and simple processing.^[29,35,36] These materials have been used for a wide range of energy storage and conversion applications, such as metal ion batteries, supercapacitors and water electrolyzers.[37-40] The chemistry of these electrodes is critical for the device performance, as they are based on intercalation of metal ions or on surface-mediated catalytic processes.[41,42]

Moreover, combination of PB and PBA with other materials can be used to obtain multifunctional electrodes or photoelectrodes.^[43] These nanocomposites can be designed to have properties that emerge from the interaction between the discrete chemical species, the oxide interface and its structural organization.^[44] In this regard, the use of transition metal oxide based mesoporous thin films of titania, ceria and zirconia, pose a high interest. Their high surface area and interconnected pore system turns them attractive as structural materials; while their band gap energy and transparency in the visible range makes them suitable for photoassisted reactions.^[45] As a result, these nanocomposites have already shown a wide range of applications^[46–48] and have potential for many more.

On the synthetic approach, one of the most appealing characteristics of CP is that they can be readily deposited on surfaces through the widely used successive ionic layer adsorption and reaction (SILAR) procedure.[49,50] This method allows excellent control in every step of the synthesis, even when introducing tuning points like ligands or ions. As mentioned above, deposition of a CP over a high surface area substrate could boost the catalyst capabilities. Also, their surface reactivity allows for further functionalization, opening a vast range of possibilities to design new composites.[51-54] In this sense, the use of SILAR on metal oxides substrates can be enhanced by applying a first molecular layer that promotes nucleation and direct CP growth through specific interactions, like coordination or π -stacking. The result is a controlled synthetic procedure and a material with reproducible properties.

Results and Discussion

Material synthesis and characterization

Mesoporous TiO₂ thin films were prepared by sol-gel methodology, using a triblock copolymer as template for the pores.^[55,56] This procedure leads to a crack-free MTTF, with a highly organized array of 8 nm diameter pores with an Im3m cubic structure,^[57] 50% pore volume and 150 nm thickness (See Experimental Section for details). The composites were synthesized using the SILAR technique, which allowed a controlled growth of the CP. This simple approach consists of several consecutive steps, schematized in Figure 1. In the first step the oxide surface is modified with the bifunctional ligand 1,10phenanthroline-5,6-dione (hereafter, pd) that serves as a surface anchor for CP growth. In the second step, the film is immersed in an Fe(II) solution, which binds to the surface attached pd. In the next step $[Fe(CN)_6]^{3-}$ is attached to Fe(II) through the cyanide bridge. From there on, SILAR cycles involve immersion on Co(II) or Fe(II) solution, followed by immersion on the [Fe(CN)₆]³⁻ solution. After every step, the film was water-rinsed to remove excess reagents. The formation of clusters on the external surface was minimized by carefully cleaning the sample with optical paper after each SILAR cycle.^[58] Repeating the SILAR cycles allows controlling the CP amount to obtain PB@MTTF and CoPBA@MTTF films.

Influence of the molecular linker

The use of the molecular linker **pd** is crucial for obtaining an ordered and controlled deposition of PB within the mesoporous structure. As described for similar ligands,^[59-61] the carbonyl groups bind to the Ti(IV) surface sites, generating a layer in which the N,N'-phenanthroline functionality remains available to coordinate transition M(II) metal ions (Figure S1).^[62] Figure 2**A**–**D** shows scanning electron microscopy (SEM) images of film surfaces following 4 SILAR cycles, comparing composites prepared with and without **pd**. In Figure 2**A**, PB synthesis was conducted without the presence of the molecular linker **pd**. This image reveals the characteristic mesoporous structure of the MTTF, albeit with small irregular particles on top of the film. Moving to Figure 2**B**, we observe that the particles are not

In this work we present the synthesis of electroactive nanocomposites of PB and its cobalt analogue (CoPBA) inside the pores of mesoporous titania thin films (MTTF). The materials were prepared through a SILAR approach, using the bifunctional ligand 1,10-phenanthroline-5,6-dione (**pd**) for titania surface functionalization. This ligand acts as nucleation center for PB and CoPBA and enhances growth inside the pores. Resulting nanocomposites are highly tunable, robust, and present good electroactive properties. Furthermore, we demonstrate that CoPBA shows catalytic activity for water oxidation that could be advantageously used in the production of solar fuels.





 $\label{eq:Figure 1.} \ensuremath{\mathsf{Sheme}}\xspace of the \ensuremath{\mathsf{SILAR}}\xspace synthesis of \ensuremath{\mathsf{PB}}\xspace \ensuremath{\mathsf{@MTTF}}\xspace nanocomposites.$



Figure 2. Figure 2. Top-view SEM images for PB@MTTF nanocomposites, (A, B) prepared without pd after 4 SILAR cycles and (C–F) with pd after 4, 6 and 8 cycles. Insets show schemes representing pore filling with PB.

homogeneous, and they are scattered across the MTTF, covering the entire sample surface. Figures 2C-D and Figure S2 feature samples where PB synthesis was carried out with the incorporation of **pd** as the first step. In this scenario, the mesoporous structure is clearly discernible, devoid of any surface particles (Figure 2D). Moreover, Figure 2C provides an extended view of the same sample, reaffirming the absence of particles above the mesopores. In essence, our results reveal that in the absence of the molecular linker **pd**, PB growth extends beyond the mesopores, leading to particle formation on the MTTF surface. This demonstrates that the surface molecular linker is crucial for the confined growth of PB within the mesoporous framework. Increasing the number of SILAR cycles leads to a tunable filling of the mesopores, as shown in Figure 2**E**–**F**. The mesoporous structure is clearly visible until the 8th SILAR cycle, after which the pores are filled up. Here, a granular morphology typical of PB films deposited over non-porous substrates appears.^[63]

The chemical composition of PB@MTTF after 6 SILAR cycles was analyzed using XPS measurements. Figure 3 shows the



0990682c



Figure 3. Fe 2p_{3/2} and N 1s XPS spectra of PB@MTTF composites and the corresponding deconvolution of the peaks.

Fe 2p_{3/2} and N 1s XPS spectra corresponding to PB@MTTF. The Fe 2p_{3/2} spectrum shows one contribution at low binding energy and a broad peak consisting of two contributions at higher energies. Thus, the spectrum could be fitted with three peaks at 708.4, 710.8 and 712.7 eV. The peak at 708.8 eV corresponds to Fe(II) while the peaks at 711.2 and 713.1 eV are due to the multiplet splitting expected for the Fe(III) ions.[64,65] The N 1s region shows two main contributions. The low binding energy peak at 397.5 eV is due to the CN⁻ group,^[65] whereas the main peak at 399.9 eV is due to the pyridinic N in the pd ligand.^[66] An extra peak at 401.2 eV could be added to account for the nitrogen atoms in the **pd** ligand coordinated to Fe ions. Note that attachment of Fe(II) to pd ligands should increase the N 1s binding energy.^[67] The intensity ratio between the pyridinic N (399.9 eV) and N-Fe (401.2 eV) peaks shows that most of the **pd** ligand is in its free form. In addition, the N_{pd} to N_{CN} intensity ratio is 3.9:1, indicating that there is one CN⁻ group for every two pd molecules. These two facts together imply that the PB@MTTF film does not grow uniformly, instead we suggest that growth proceeds via the formation of clusters that start growing at the sites where the pd ligand is coordinating an Fe(II) ion.

PB growth

The growth of PB@MTTF was studied using UV-vis spectroscopy. The appearance of a deep-blue color in the film is indicative of the nanocomposite formation (Figure S3).^[68] The origin of this coloration is the metal-to-metal charge transfer (MMCT) band of the polymeric [Fe^{II}-CN-Fe^{III}] sequences, observed at 695 nm in the spectra shown in Figure 4**A**, the same as for bulk PB.^[69] Even for the first growth cycle, the band is already noticeable thanks to the incorporation of a considerable amount of the CP on the large specific area of the MTTF. With an increase in the number of SILAR cycles, the MMCT absorption band becomes more intense, showing a linear relation with the number of cycles, indicating that roughly the same amount of PB is incorporated in each cycle (Figure 4**B**). After the 8th cycle, the absorbance growth is still linear, but the increase between successive cycles becomes smaller.

FTIR spectra were also used to follow film growth, making use of the strong absorption around 2080 cm⁻¹ characteristic of the C \equiv N bond. PB@MTTF spectra showed an increase in absorbance at 2086 cm⁻¹ with the increase of SILAR cycles (Figure 4**C**, **D**). The infrared absorbance follows the same behavior as the one observed with UV–Vis spectroscopy: a linear increase in the first seven cycles, levelling off after the 8th SILAR cycle.

The change in pore accessibility of PB@MTTF with different number of SILAR cycles was quantified using X-ray reflectometry (XRR) measurements (Figure S4). The MTTF sample shows a clear displacement in its critical angle when humidity is increased. From these measurements, an accessible porosity of 50% is calculated, which is in good agreement with previous results in similar systems.^[56] When PB is deposited over MTTF, the accessible porosity decreases. Indeed, Table 1 shows that as the number of SILAR cycles increases, the accessible porosity decreases, reaching 5% after 9 SILAR cycles due to PB filling.^[70] This is an indication of the progressive filling of the MTTF pores.

Table 1. Accessible porosity for PB@MTTF with different number of SILAR cycles.				
N° SILAR cycles	Acc. Porosity [%]			
0	50			
3	17			
6	10			
9	5			

0990682c,



Figure 4. UV–Vis spectra of PB@MTTF nanocomposites with increasing number of SILAR cycles (**A**), and absorption at the maximum (Abs₆₉₅) vs number of SILAR cycles (**B**). FTIR absorption spectra for PB@MTTF, showing the v_{CN} band as a function of SILAR cycles (**C**) and absorbance at 2086 cm⁻¹ as a function of SILAR cycles (**D**).

Nonetheless, the pore network is still accessible, particularly for a low number of cycles. From nine cycles and beyond, the remaining porosity is probably due to PB particles roughness.

The obtained results suggest a two-step growth process of PB on MTTF. A schematic representation of this process is shown in Figure 5. During the first SILAR cycles, PB growth within the mesopores is favored due to preconcentration^[71] and increased surface areas of the empty pores (Figure 5**B** 1–**3**). This leads to a large increase in the amount of PB deposited, as seen with UV–vis and FTIR spectroscopies. When the pores are filled up, the available surface area is much smaller. This results in a significant decrease in the amount of PB incorporated in each cycle, leading to a change in slope and morphology after the 8th SILAR cycle. (Figure 5**B** 4).

Electrochemical performance: connectivity within the pores

The high surface area and controllable accessible porosity of MTTF are unique features that can be exploited in the generation of catalytically active nanocomposites. For PBA@MTTF nanocomposites, the pore space is still accessible, as determined by XRR, and a high interface is achieved. Therefore, electrochemical currents are expected to be higher than those observed in low surface area substrates. This feature is particularly relevant in the development of intercalation batteries,^[38] sensors^[72,73] and catalysts.^[45]

A typical cyclic voltammogram of PB@MTTF prepared using 4 SILAR cycles is presented in Figure 6. Redox peaks are observed at $E_{1/2}$ = 214 mV and 873 mV in this case.



Figure 5. Scheme of the absorbance response on SILAR cycles (**A**) and a corresponding idealized model of PB growth within the mesopores (**B**). The molecular linker **pd** binds to the TiO_2 walls. After the first SILAR cycle (1), Fe^{2+} binds to some of the free pb linkers and $Fe(CN)_6^{3-}$ binds to it, forming the first nuclei for PB formation. After several SILAR cycles, PB grows on these nuclei (2). With each SILAR cycle, PB particles grow leading to a linear increase in absorbance. After 8 cycles, the pores are filled up (3). Further SILAR cycles lead to PB formation on top of the MTTF (4), and a lower increase in absorbance.



Figure 6. Cyclic voltammogram of PB@MTTF nanocomposite prepared using 4 SILAR cycles. Scan rate 50 mV.s⁻¹ in pH 7 phosphate buffer.

The observed behavior is similar to that described for the bulk materials,^[74,75] but with slightly shifted redox potentials. The PB@MTTF nanocomposite shows the two known redox processes in the explored window of potentials. PB (Fe^{II}-Fe^{III}) is reduced to form Prussian White [Fe^{II}-Fe^{II}, Eq. (1)] at cathodic potentials (E < 214 mV), while in the anodic region (E > 873 mV) PB is fully oxidized [Fe^{III}-Fe^{III}, Eq. (2)].^[68]

$$\begin{split} & Fe^{III}{}_{4}[Fe^{II}(CN)_{6}]_{3} + 4 \; e^{-} + 4 \; K^{+} \rightleftharpoons K_{4}Fe^{II}{}_{4}[Fe^{II}(CN)_{6}]_{3} \\ & E_{1/2} = 214 \; mV, \; E_{1/2\text{-bulk}} = 234 \; mV \end{split} \tag{1}$$

$$\begin{split} & \mathsf{Fe}^{III}_{\,\,4}[\mathsf{Fe}^{II}(\mathsf{CN})_6]_3 + 3 \; \mathsf{NO}_3^{\,-} \rightleftharpoons 3 \; \mathsf{e}^- + \mathsf{Fe}^{III}_{\,\,4}[\mathsf{Fe}^{III}(\mathsf{CN})_6]_3(\mathsf{NO}_3)_3 \\ & \mathsf{E}_{1/2} = 873 \; \mathsf{mV}, \; \mathsf{E}_{1/2\text{-bulk}} = 909 \; \mathsf{mV} \end{split} \tag{2}$$

The use of transparent MTTF electrodes enabled the spectroelectrochemical investigation of the nanocomposites under cycling.^[76] The spectroelectrochemistry of PB@MTTF allowed us to further characterize the cathodic peak, where the reduction is accompanied by bleaching in the visible part of the spectra due to the loss of the MMCT transition (Figure S5).

The fact that redox bands are observed for each species shows that the immobilized Prussian blue presents electrical communication. For moieties anchored to the surface of insulating materials, electron transfer usually occurs through an electron hopping mechanism between neighboring sites. The higher the density of surface groups, the higher the current achieved.^[77] Semiconductor substrates, such as titania, also improve electron transfer. Electrolyte ions diffusion is needed in order to maintain charge balance and, when diffusion is fast enough and does not become the rate determining step, peak currents are proportional to the scan rate.^[78] If diffusion is slow, peak currents show a linear behavior with the square root of scan rate.^[79] For PB@MTTF, peak currents have a linear relationship with the increase in the scan rate from 5 mV.s^{-1} to 400 mV.s⁻¹, as can be observed in Figure 7 (R²=0.992). Furthermore, no linearity is observed with the square root of the scan rate (Figure S6). This is further evidence that PB is immobilized in the pore walls of MTTF. Also, peak-to-peak separation grows with the scan rate, while $E_{1/2}$ is independent, which is analogous to what was previously reported for similar immobilized materials.[80]

The stability of the PB@MTTF composites was studied through cyclization around each redox process independently. The results for PB@MTTF after 4 SILAR cycles are shown in Figure S7. The process at lower potential is completely reversible and retains its current even after 15 cycles, while cycling around the oxidation process results in a significant current intensity decrease, suggesting that desorption occurs to some degree.

Each SILAR cycle results in an increase in peak current due to the higher PB loading (Figure S8). The peak current of the cathodic peak grows linearly with the number of cycles until the 8th SILAR cycle, when the pores are filled up. This behavior correlates with the one observed by UV-Vis and FTIR spectroscopies. Also, peak-to-peak separation for both redox processes in PB@MTTF gets larger with each SILAR cycle, with a sharp increase from the 6th cycle onwards (Table 2). A smaller peak separation indicates a more reversible electron transfer process. A less reversible process takes place with more layers, i.e., when the content of PB increases. This could be related to the need for cation insertion during the reduction of PB, essential in maintaining electroneutrality. Cation insertion in PB results in a structural deformation (expansion), as well as a distinct electrochemical response when changing the electrolyte from KNO₃ to NaNO₃, as reported in the literature.^[81] The same dependence



Figure 7. Voltammogram at different scan rates of PB@MTTF, 4 SILAR cycles, in pH 7 phosphate buffer (A); peak current vs scan rate for the same film (B).

Chemistry Europe

European Chemical Societies Publishing

Table 2. Peak to peak separation for PB@MTTF redox potentials (ΔE , in mV).								
Number of SILAR cycles	2	3	4	5	6	7	8	
$\Delta E (E_{1/2} = 214 \text{ mV})$	33.6	41.6	52.6	43.9	103.6	114.5	159.5	
ΔE (E _{1/2} =873 mV)	35.5	45.6	54.5	53.8	142.6	119.5	169.5	

was observed in PB@MTTF nanocomposite (Figure S9), indicating that ions permeate through the PB located within the mesoporous structure. However, as the PB film thickens, the diffusion of cations within the pore network becomes more challenging, possibly due to the significant reduction in porosity, which could ultimately limit the overall charge transfer process.

Changing M²⁺: towards an ordered OER catalyst based in CoPBA

Influence of pH in the material synthesis

For CoPBA synthesis, a CoCl₂ solution was used after the first SILAR cycle, which is performed using the $Fe(SO_4)(NH_3)_2$ solution, as Fe^{2+} binds to **pd** with higher affinity. The growth process of CoPBA@MTTF was followed by SEM and FTIR spectroscopy. UV-vis spectroscopy results are not significant in this system, as the MMCT band is less intense than in PB, leading to almost no color and thus no signal of absorbance in the composite.

When the CoCl₂ solution was used as-prepared (pH ~5), high amounts of CoPBA were deposited, forming large cubic nanoparticles on top of the mesostructured film, which is undesirable (Figure 8**A**–**B**). To favor a highly controlled deposition within the pores, the solution pH was changed to 4, a pH closer to that measured of the Mohr salt used for PB deposition.

The pH of the solution affects the adsorption and formation of the CP because several acid-base equilibria are involved, and the TiO_2 surface –OH density, **pd** protonation and $Co^{2+}(aq)$ speciation depend on pH. These features change the interaction of the metal ion with the pore surface and affect the adsorption rate.

For CoPBA@MTTF grown at pH 4, the intensity of the v_{CN} band in the IR spectrum follows a linear increase with the number of SILAR cycles. Intensity is smaller than for PB@MTTF, but its controlled and steady increment indicates that the composite is growing (Figure 8C). This procedure resulted in a composite material with almost no particles on the surface (Figure 8D). In this case, no change of slope is observed in FTIR measurements, indicating that the pore saturation is not achieved within the number of SILAR cycles performed. These results show the critical influence of the solution pH during cation adsorption in the controlled formation of CoPBA within the mesopores. Higher pH leads to formation of cubic nanoparticles on top of the MTTF, as seen in Figure 8B, while a lower pH allowed us to avoid this.

Electrochemical performance

Cyclic voltammograms of CoPBA@MTTF prepared using 4 SILAR cycles are shown in Figure 9. The CoPBA@MTTF nanocomposite shows two different redox processes at $E_{1/2}$ =296 mV and 756 mV. Upon the formation of CoPBA, an internal electron



Figure 8. FTIR absorbance spectra showing the v_{CN} band and absorbance at 2108 cm⁻¹ as a function of SILAR cycles and SEM top-view for CoPBA@MTTF grown by direct dissolution of CoCl₂ (**A**, **B**) and after adjusting the solution pH to 4 (**C**, **D**).



Figure 9. (A) Cyclic voltammogram of the CoPBA@MTTF nanocomposite, 4 SILAR cycles, grown at pH 4, scan rate 50 mV.s⁻¹ in pH 7 phosphate buffer. (B) Oxygen evolution catalysis at bare MTTF, 4 SILAR cycles CoPBA@MTTF before and after extra Co²⁺ incorporation.

transfer from Co(II) to $[Fe(CN)_6]^{3-}$ occurs, generating the mixedvalence form of CoPBA (Co^{III}Fe^{II}). Then, the reduction to Co(II) is assigned to the cathodic peak, as previously described.^[75] On the other hand, the peak at higher potentials is assigned to the oxidation of the $[Fe^{II}(CN)_6]^{4-}$ moiety to form the fully oxidized form (Co^{III}Fe^{III}).

Films of Cobalt Prussian Blue Analogue deposited over different substrates have shown to be active for the oxidation of water in neutral media,^[33,82–85] and CoPBA@MTTF composites are not an exception. Figure 9A shows the cyclic voltammetry of CoPBA@MTTF at pH 7. A catalytic wave is observed at high oxidation potentials (>1.2 V), which is attributed to oxygen evolution. Figure 9B shows the comparison between bare MTTF and a CoPBA@MTTF with 4 SILAR cycles. An additional immersion of the film into the CoCl₂ solution increases the obtained current while also decreasing the onset oxidation potential (E_{onset} = 1.28 V for CoPBA@MTTF and 1.25 V for CoPBA@MTTF with an extra immersion in Co(II) solution, Figure S10). The additional Co ions incorporated in the last step certainly do not present a saturated coordination sphere, and these extra open coordination sites can act as additional catalytic sites for the water oxidation reaction. The measured onset potential is consistent with previous studies on CoPBA^[33] (E_{onset} ~1.26 V), although the current observed at these potentials is lower. We attribute this discrepancy to the considerably lower loading of the catalytic material in our films, which could be further optimized for higher currents in future work.

Conclusions

Nanocomposites made up of Prussian blue and its cobalt analogue CoPBA embedded within mesoporous titania thin films were obtained through a simple, soft and highly tunable SILAR treatment. We also showed the important influence of a surface linker species (**pd**) used as a controller of PB nucleation within the mesopores. This led to a smooth and continuous pore filling. The multi-technique characterization allowed a full portrayal of these materials obtained by different synthetic

procedures, from finely tuned pore loading with PB@MTTF or CoPBA@MTTF to surface segregated particles. Surface modification of the MTTF porous structure permits to tune PB growth in a stepwise and controlled way, where material properties change smoothly and in a controllable fashion as the mesopores are filled up. Furthermore, these nanocomposites are electroactive and transparent while retaining their porous structure, making them attractive for future electro- and photoelectrocatalytic applications. PB@MTTF in particular could be further studied for intercalation batteries, while CoPBA@MTTF presents an interesting catalytic activity toward oxygen evolution that could be further optimized. The flexibility of this PBA@MTTF platform allows for the incorporation of any labile transition metal ion or fragment into the structure of the coordination polymer and into the mesopores. Thus, this work provides the reproducible procedures for the design and synthesis of a family of composites made up of a straightforward combination of mesoporous materials and coordination polymers that can be the base for (photo)electrochemical devices. Having demonstrated electroactivity and connectivity of the metal centers towards OER, future work is aimed at an indepth study of nanocomposite photoanodes produced through this simple, tunable, and reproducible route, with solar fuel production as target application.

Experimental Section

All chemicals were reagent grade and used without further purification. TiCl₄, non-ionic block-copolymer Pluronic F127 ((PEO)₁₀₆(PPO)₇₀(PEO)₁₀₆ where PEO=poly(ethylene oxide) and PPO=poly(propylene oxide)) and absolute ethanol were purchased from Merck. 1,10-phenanthroline, K₃[Fe(CN)₆], concentrated HCl and CoCl₂·6 H₂O were purchased from Sigma–Aldrich. Fe(NH₄)₂(SO₄)₂·6 H₂O, K₂HPO₄ and KH₂PO₄ were purchased from Biopack. Glass substrates were purchased from Biotraza, indium tin oxide (ITO) coated glass was purchased from Marienfeld-Superior, fluorine-doped tin oxide (FTO) coated glass was purchased from Delta Technologies and silicon wafers were purchased from University Wafer. All solutions were prepared using Milli-Q water (Elga System UHQ, 18 MΩ cm⁻¹). The ligand 1,10-phenanthroline-5,6-dione (**pd**) was prepared according to literature procedures.^[86]

MTTF were synthesized onto different substrates according to literature procedures.^[56,87] Briefly, initial sols were obtained by mixing TiCl₄, ethanol, copolymer template Pluronic F127 and water in a 1:40:5×10⁻³:10 molar ratio. Films were deposited by dipcoating on clean glass substrates, ITO coated glass or silicon wafers at 30°C, 25–30% relative humidity (RH) and 2.0 mm.s⁻¹ withdrawal rate. As-prepared films were aged 24 h at 50% RH. Further thermal treatment was performed by heating 24 h at 60°C, 24 h at 130°C and 2 h at 350°C, with a heating ramp of 1°C.min⁻¹.

PB growth on MTTF

The preparation of confined Prussian Blue (Fe₃[Fe(CN)₆]₂; PB@MTTF) and its cobalt analogue (Co4[Fe(CN)6]3; CoPBA@MTTF) was done using a successive ionic layer adsorption and reaction (SILAR) approach based on previous work.[57,58] MTTF films were first immersed overnight in a 5 mM solution of pd in ethanol and then 30 min in pure ethanol to remove the non-specifically bound ligand. This procedure forms the anchoring ligand layer. The pdfunctionalized films were then immersed for 30 min in a 50 mM solution of Fe(NH₄)₂(SO₄)₂.6 H₂O, followed by rinsing with water and immersed for another 30 min in a 50 mM solution of K₃[Fe(CN)₆]. Afterwards, the film surface was gently cleaned with optical paper to remove superficial particles and to avoid growth outside the mesopores. To continue the CP growth, a new immersion in a 50 mM solution of M(II) (either Fe(NH₄)₂(SO₄)₂.6 H₂O or CoCl₂.6 H₂O) for 30 min was done. Two different treatments were made for obtaining the CoPBA@MTTF. The first was performed by dissolving cobalt chloride in water, while the second was done by acidifying the same solution to pH = 4.0 with HCl (c). Finally, in both cases, the films were rinsed with water and immersed for another 30 min in a 50 mM solution of K_3 [Fe(CN)₆] and the film surface was cleaned.

Materials characterization

The growth progress of the composite material on glass or ITO substrates was monitored through UV–Vis absorption spectroscopy on an HP8453 Hewlett-Packard spectrophotometer. The spectra measurements were made by immersing the film in ethanol, using a Teflon piece designed to hold it inside a quartz cuvette controlling the exposed area.

FTIR absorption spectra for composite growth analysis were collected on the thin films deposited onto silicon wafer substrates, using a Nicolet FTIR 510P spectrometer.

Field Emission Scanning Electron Microscopy (FE-SEM) images were obtained on an SEM Zeiss Supra 40 equipped with a field emission gun from CMA – FCEN-UBA.

X-ray photoelectron spectroscopy (XPS) measurements were made in an ultrahigh vacuum (UHV) chamber. The chamber is equipped with a monochromatic Al K α X-ray source and a hemispherical SPECS electron energy analyzer. PB@MTTF with 6 SILAR cycles on ITO coated glass was used for these measurements.

X-ray reflectometry (XRR) measurements were performed on a Panalytical Empyrean X-ray diffractometer with an incident beam of Cu K α radiation at 1.54 Å. A divergence slit of 0.05 mm and a mask of 10 mm were used for the measurements.^[88] The samples accessible porosities was calculated from XRR data by measuring the change in the critical angle (indicative of the thin film electronic density) when the RH changes from <5% (*i.e.* the pores are full of air) to >90% (*i.e.* the pores are filled with water). For that purpose, first the films were carefully dried at 60°C and kept under dry

atmosphere. XRR measurements were performed using a chamber whose humidity was controlled by introducing silica gel (to decrease RH) or boiling water (to increase RH).

The increment in the film density at high RH values was considered only due to the water content in the pores. After this assumption, the water volume fraction ($F_v(H_2O)$) within the film was determined from the measured electronic densities using Equation (3). Under this conditions, the calculated $F_v(H_2O)$ is equivalent to the accessible porosity (P) of the material.

$$P = F_{v}(H_{2}O) = \frac{\rho_{e}(film + H_{2}O) - \rho_{e}(film)}{\rho_{e}(H_{2}O)}$$
(3)

where $\rho_e(film + H_2O)$ is the electronic density of water-filled film (measured at high RH), $\rho_e(film)$ is the electronic density of the film (measured at low RH) and the $\rho_e(H_2O)$ is the water electronic density.

Electrochemical experiments were performed with a TEQ V3.0 potentiostat from nanoTEQ and TEQ_03 software. A standard threeelectrode array was used, consisting of a platinum mesh counter electrode, Ag/AgCl/KCl 3 M electrode as reference and PB@MTTF or CoPBA@MTTF on ITO coated glass as the working electrode. Supporting electrolyte was KNO₃ 1 M in 50 mM pH 7 phosphate buffer. Spectroelectrochemical measurements were made using a silver wire as reference instead, with UV–Vis absorption spectra recorded on an HP8453 Hewlett-Packard spectrophotometer. The film was supported in the cuvette by a Teflon piece adapted to hold the reference and counter electrodes.

The onset potential for OER was estimated as the intersection between the linear extrapolation of the catalytic current and the current before the sudden increase. For comparison, data was extracted from Ref. [35] (Figure 3) and the E_{onset} was estimated in the same way.

Acknowledgements

This work was financially supported by ANPCyT (PICT 2015-0351, PICT 2017-1028, 2017-1133, 2017-4651, 2018-04236, 2020-03130), UBA (UBACyT 20020130100534BA), CONICET (PIP GI 11220210100917CO) and UNSAM. P.V. thanks UBA for the Estímulo scholarship. P.V., R. M. C., E. T. and C. C. F. thank CONICET for their fellowship grants. P. C. A., M. C. F., F. J. W., G. J. A. A. S. I., and L. M. B. are members of CONICET.

Conflict of Interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords: Energy conversion • mesoporous materials • Prussian Blue Analogues • supported catalysts • water splitting

- [1] G. P. Peters, R. M. Andrew, T. Boden, J. G. Canadell, P. Ciais, C. Le Quéré, G. Marland, M. R. Raupach, C. Wilson, *Nat. Clim. Change* 2013, 3, 4–6.
- [2] L. C. King, J. C. J. M. van den Bergh, *Nat. Energy* **2018**, *3*, 334–340.
- [3] A. B. Gallo, J. R. Simões-Moreira, H. K. M. Costa, M. M. Santos, E. Moutinho dos Santos, *Renewable Sustainable Energy Rev.* 2016, 65, 800–822.
- N. Y. Murakami Iha, T. J. Meyer, *Pure Appl. Chem.* **2011**, *83*, 749–768. [6] Y. Yang, S. Ajmal, X. Zheng, L. Zhang, *Sustain. Energy Fuels* **2018**, *2*, 510–537.
- [7] Y. Liang, Y. Yao, Nat. Rev. Mater. 2023, 8, 109–122.
- [8] R. B. Gupta, Hydrogen Fuel: Production, Transport, and Storage, Crc Press, 2008.
- [9] F. Barbir, Sol. Energy 2005, 78, 661–669.
- [10] J. D. Holladay, J. Hu, D. L. King, Y. Wang, Catal. Today 2009, 139, 244– 260.
- [11] S. Ardo, D. Fernandez Rivas, M. A. Modestino, V. Schulze Greiving, F. F. Abdi, E. Alarcon Llado, V. Artero, K. Ayers, C. Battaglia, J.-P. Becker, D. Bederak, A. Berger, F. Buda, E. Chinello, B. Dam, V. Di Palma, T. Edvinsson, K. Fuji, H. Gardeniers, H. Geerlings, S. M. H. Hashemi, S. Haussener, F. Houle, J. Huskens, B. D. James, K. Konrad, A. Kudo, P. P. Kunturu, D. Lohse, B. Mei, E. L. Miller, G. F. Moore, J. Muller, K. L. Orchard, T. E. Rosser, F. H. Saadi, J.-W. Schüttauf, B. Seger, S. W. Sheehan, W. A. Smith, J. Spurgeon, M. H. Tang, R. van de Krol, P. C. K. Vesborg, P. Westerik, *Energy Environ. Sci.* 2018, *11*, 2768–2783.
- [12] S. W. Boettcher, ACS Energy Lett. 2020, 5, 70-71.
- [13] A. Fujishima, K. Honda, Nature 1972, 238, 37–38.
- [14] J. Rossmeisl, Z.-W. Qu, H. Zhu, G.-J. Kroes, J. K. Nørskov, J. Electroanal. Chem. 2007, 607, 83–89.
- [15] S. Bae, J.-E. Jang, H.-W. Lee, J. Ryu, Eur. J. Inorg. Chem. 2019, 2019, 2040– 2057.
- [16] C. C. L. McCrory, S. Jung, J. C. Peters, T. F. Jaramillo, J. Am. Chem. Soc. 2013, 135, 16977–16987.
- [17] J. J. Concepcion, J. W. Jurss, M. K. Brennaman, P. G. Hoertz, A. O. T. Patrocinio, N. Y. Murakami Iha, J. L. Templeton, T. J. Meyer, Acc. Chem. Res. 2009, 42, 1954–1965.
- [18] L. Duan, Y. Xu, P. Zhang, M. Wang, L. Sun, *Inorg. Chem.* **2010**, *49*, 209–215.
- [19] J. D. Blakemore, N. D. Schley, D. Balcells, J. F. Hull, G. W. Olack, C. D. Incarvito, O. Eisenstein, G. W. Brudvig, R. H. Crabtree, *J. Am. Chem. Soc.* 2010, *132*, 16017–16029.
- [20] R. Matheu, M. Z. Ertem, C. Gimbert-Suriñach, X. Sala, A. Llobet, Chem. Rev. 2019, 119, 3453–3471.
- [21] J. Wang, Y. Gao, H. Kong, J. Kim, S. Choi, F. Ciucci, Y. Hao, S. Yang, Z. Shao, J. Lim, Chem. Soc. Rev. 2020, 24, 9154–9196.
- [22] C. C. L. McCrory, S. Jung, I. M. Ferrer, S. M. Chatman, J. C. Peters, T. F. Jaramillo, J. Am. Chem. Soc. 2015, 137, 4347–4357.
- [23] B. M. Hunter, H. B. Gray, A. M. Müller, Chem. Rev. 2016, 116, 14120– 14136.
- [24] I. Roger, M. A. Shipman, M. D. Symes, Nat. Chem. Rev. 2017, 1, 0003.
- [25] K. Maeda, K. Domen, J. Phys. Chem. Lett. 2010, 1, 2655-2661.
- [26] Q. Wang, K. Domen, Chem. Rev. 2020, 120, 919–985.
- [27] X. Meng, S. Xu, C. Zhang, P. Feng, R. Li, H. Guan, Y. Ding, Chem. Eur. J. 2022, 28, e202201407.
- [28] C. Janiak, Dalton Trans. 2003, 14, 2781.
- [29] X. Roy, M. J. MacLachlan, Chem. Eur. J. 2009, 15, 6552–6559.
- [30] L.-M. Cao, D. Lu, D.-C. Zhong, T.-B. Lu, Coord. Chem. Rev. 2020, 407, 213156.
- [31] C. Deng, D. Wang, Batteries & Supercaps 2019, 2, 290–310.
- [32] Q. Gao, J. Chen, Q. Li, J. Zhang, Z. Zhai, S. Zhang, R. Yu, X. Xing, Inorg. Chem. Front. 2018, 5, 438–445.
- [33] S. Pintado, S. Goberna-Ferrón, E. C. Escudero-Adán, J. R. Galán-Mascarós, J. Am. Chem. Soc. 2013, 135, 13270–13273.
- [34] E. P. Alsaç, E. Ülker, S. V. K. Nune, Y. Dede, F. Karadas, Chem. Eur. J. 2018, 24, 4856–4863.
- [35] J. Guo, H. Li, D. Wang, L. Zhang, Y. Ma, N. Akram, Y. Zhang, J. Wang, Catal. Sci. Technol. 2018, 8, 6375–6383.
- [36] X. Su, Y. Wang, J. Zhou, S. Gu, J. Li, S. Zhang, J. Am. Chem. Soc. 2018, 140, 11286–11292.

- [37] J. Chen, L. Wei, A. Mahmood, Z. Pei, Z. Zhou, X. Chen, Y. Chen, *Energy Storage Mater.* 2020, 25, 585–612.
- [38] H. Yi, R. Qin, S. Ding, Y. Wang, S. Li, Q. Zhao, F. Pan, Adv. Funct. Mater. 2021, 31, 2006970.
- [39] Y. Bai, K. YuChi, X. Liu, S. Tian, S. Yang, X. Qian, B. Ma, M. Fang, Y. Liu, Z. Huang, X. Min, *Eur. J. Inorg. Chem.* **2023**, *26*, e202300246.
- [40] W. Sun, Z. Wei, J. Qi, L. Kang, J. Li, J. Xie, B. Tang, Y. Xie, Chin. J. Chem. 2021, 39, 2347–2353.
- [41] A. Mehdi, C. Reye, R. Corriu, Chem. Soc. Rev. 2011, 40, 563-574.
- [42] R. M. Caraballo, D. Onna, N. López Abdala, G. J. A. A. Soler Illia, M. Hamer, Sens. Actuators B 2020, 309, 127712.
- [43] T. G. Ulusoy Ghobadi, E. Ozbay, F. Karadas, Chem. Eur. J. 2021, 27, 3638– 3649.
- [44] P. Gómez-Romero, C. Sanchez, Eds., Functional Hybrid Materials, Wiley, 2003.
- [45] N. Linares, A. M. Silvestre-Albero, E. Serrano, J. Silvestre-Albero, J. García-Martínez, Chem. Soc. Rev. 2014, 43, 7681–7717.
- [46] X. Chen, S. S. Mao, Chem. Rev. 2007, 107, 2891–2959.
- [47] F. E. Osterloh, Chem. Mater. 2008, 20, 35-54.
- [48] A. Walcarius, Chem. Soc. Rev. 2013, 42, 4098.
- [49] M. H. Beyzavi, N. A. Vermeulen, K. Zhang, M. So, C.-W. Kung, J. T. Hupp, O. K. Farha, *ChemPlusChem* **2016**, *81*, 708–713.
- [50] H. J. Park, M. C. So, D. Gosztola, G. P. Wiederrecht, J. D. Emery, A. B. F. Martinson, S. Er, C. E. Wilmer, N. A. Vermeulen, A. Aspuru-Guzik, J. F. Stoddart, O. K. Farha, J. T. Hupp, ACS Appl. Mater. Interfaces 2016, 8, 24983–24988.
- [51] U. Diebold, Surf. Sci. Rep. 2003, 48, 53-229.
- [52] E. H. Otal, P. C. Angelomé, S. A. Bilmes, G. J. A. A. Soler-Illia, Adv. Mater. 2006, 18, 934–938.
- [53] H. Wang, A. S. Adeleye, Y. Huang, F. Li, A. A. Keller, Adv. Colloid Interface Sci. 2015, 226, 24–36.
- [54] H. Kim, M. Kim, W. Kim, W. Lee, S. Kim, J. Hazard. Mater. 2018, 357, 449– 456.
- [55] G. J. A. A. Soler-Illia, P. Vensaus, D. Onna, in *Chem. Solut. Synth. Mater. Des. Thin Film Device Appl.*, Elsevier, 2021, pp. 195–229.
- [56] G. J. A. A. Soler-Illia, P. C. Angelomé, M. C. Fuertes, D. Grosso, C. Boissiere, *Nanoscale* 2012, 4, 2549.
- [57] M. Gaitán, V. R. Gonçales, G. J. A. A. Soler-Illia, L. M. Baraldo, S. I. C. de Torresi, *Biosens. Bioelectron.* 2010, *26*, 890–893.
- [58] A. Fischereder, M. L. Martinez-Ricci, A. Wolosiuk, W. Haas, F. Hofer, G. Trimmel, G. J. A. A. Soler-Illia, *Chem. Mater.* 2012, 24, 1837–1845.
- [59] I. A. Janković, Z. V. Šaponjić, M. I. Čomor, J. M. Nedeljković, J. Phys. Chem. C 2009, 113, 12645–12652.
- [60] W. R. McNamara, R. C. Snoeberger, G. Li, J. M. Schleicher, C. W. Cady, M. Poyatos, C. A. Schmuttenmaer, R. H. Crabtree, G. W. Brudvig, V. S. Batista, J. Am. Chem. Soc. 2008, 130, 14329–14338.
- [61] P. C. Angelomé, G. J. de A. A. Soler-Illia, Chem. Mater. 2005, 17, 322-331.
- [62] C. A. Goss, H. D. Abruna, Inorg. Chem. 1985, 24, 4263-4267.
- [63] B. F. Baggio, C. Vicente, S. Pelegrini, C. C. Plá Cid, I. S. Brandt, M. A. Tumelero, A. A. Pasa, *Materials* 2019, *12*, 1103.
- [64] A. Lisowska-Oleksiak, A. P. Nowak, M. Wilamowska, M. Sikora, W. Szczerba, C. Kapusta, Synth. Met. 2010, 160, 1234–1240.
- [65] L. Cao, Y. Liu, B. Zhang, L. Lu, ACS Appl. Mater. Interfaces 2010, 2, 2339– 2346.
- [66] P. Gayathri, A. Senthil Kumar, Langmuir 2014, 30, 10513–10521.
- [67] M. Bron, J. Radnik, M. Fieber-Erdmann, P. Bogdanoff, S. Fiechter, J. Electroanal. Chem. 2002, 535, 113–119.
- [68] D. Ellis, M. Eckhoff, V. D. Neff, J. Phys. Chem. 1981, 85, 1225-1231.
- [69] M. Pyrasch, B. Tieke, Langmuir 2001, 17, 7706–7709.
- [70] M. C. Fuertes, M. Marchena, M. C. Marchi, A. Wolosiuk, G. J. A. A. Soler-Illia, Small 2008, 5, 272–280.
- [71] G. Giménez, D. Estrin, Fabricación y caracterización de arreglos de electrodos recubiertos con películas delgadas mesoporosas de óxido de silicio y óxidos mixtos de silicio y circonio, Tesis Doctoral, Universidad de Buenos Aires. Facultad de Ciencias Exactas y Naturales, 2018.
- [72] T. Wagner, S. Haffer, C. Weinberger, D. Klaus, M. Tiemann, Chem. Soc. Rev. 2013, 42, 4036–4053.
- [73] A. Walcarius, Electroanalysis 2015, 27, 1303–1340.
- [74] K. Itaya, T. Ataka, S. Toshima, J. Am. Chem. Soc. 1982, 104, 4767–4772.
 [75] R. O. Lezna, R. Romagnoli, N. R. de Tacconi, K. Rajeshwar, J. Phys. Chem.
- *B* 2002, *106*, 3612–3621. [76] C. Renault, V. Balland, E. Martinez-Ferrero, L. Nicole, C. Sanchez, B.
- [76] C. Renault, V. Balland, E. Martinez-Perfero, L. Nicole, C. Sanchez, B. Limoges, Chem. Commun. 2009, 48, 7494.
- [77] C. Delacote, J. P. Bouillon, A. Walcarius, *Electrochim. Acta* 2006, 51, 6373–6383.

Eur. J. Inorg. Chem. 2024, 27, e202300576 (10 of 11)





10990682c

- [78] Z. Zhou, A. W. Franz, S. Bay, B. Sarkar, A. Seifert, P. Yang, A. Wagener, S. Ernst, M. Pagels, T. J. J. Müller, W. R. Thiel, *Chem. Asian J.* **2010**, *5*, 2001–2015.
- [79] S. Frasca, T. von Graberg, J.-J. Feng, A. Thomas, B. M. Smarsly, I. M. Weidinger, F. W. Scheller, P. Hildebrandt, U. Wollenberger, *ChemCatCh-em* 2010, 2, 839–845.
- [80] Z. Li, J. Chen, W. Li, K. Chen, L. Nie, S. Yao, J. Electroanal. Chem. 2007, 603, 59–66.
- [81] S. Saeed, S. Boyd, W.-Y. Tsai, R. Wang, N. Balke, V. Augustyn, Chem. Commun. 2021, 57, 6744–6747.
- [82] M. Aksoy, S. V. K. Nune, F. Karadas, Inorg. Chem. 2016, 55, 4301–4307.
- [83] B. M. Pires, P. L. Dos Santos, V. Katic, S. Strohauer, R. Landers, A. L. B. Formiga, J. A. Bonacin, *Dalton Trans.* 2019, 48, 4811–4822.
- [84] B. M. Pires, F. S. Hegner, J. A. Bonacin, J.-R. Galán-Mascarós, ACS Appl. Energ. Mater. 2020, 3, 8448–8456.

- [85] F. S. Hegner, J. R. Galán-Mascarós, N. López, J. Phys. Chem. Lett. 2022, 13, 4104–4110.
- [86] U. Udeochu, T. Jimerson, A. Vivoni, O. Bakare, C. M. Hosten, J. Phys. Chem. A 2007, 111, 3409–3415.
- [87] E. L. Crepaldi, G. J. de A. A. Soler-Illia, D. Grosso, F. Cagnol, F. Ribot, C. Sanchez, J. Am. Chem. Soc. 2003, 125, 9770–9786.
- [88] M. M. Zalduendo, J. Langer, J. J. Giner-Casares, E. B. Halac, G. J. A. A. Soler-Illia, L. M. Liz-Marzán, P. C. Angelomé, J. Phys. Chem. C 2018, 122, 13095–13105.

Manuscript received: September 18, 2023 Revised manuscript received: November 14, 2023 Accepted manuscript online: November 15, 2023 Version of record online: November 29, 2023