Introduction

Combining domains of different chemical nature within the same hybrid material through the formation of heterojunctions provides the opportunity to exploit the properties of each individual component within the same nano-object; furthermore, new synergistic properties will often arise as a result of unique interface interactions. However, synthetic strategies enabling precise control over the final architecture of multicomponent objects still remain scarce for certain classes of materials. Herein, we report on the formation of Cu/MO$_x$ (M = Ce, Zn and Zr) hybrid nanocrystals with a tunable number of interfaces between the two domains. We demonstrate that the organic ligands employed during the synthesis play a key role in regulating the final configuration. Finally, we show that the synthesized nanocrystals serve as materials platforms to investigate the impact of the Cu/metal oxide interfaces in applications by focusing on the electrochemical CO$_2$ reduction reaction as one representative example.

Results and discussion

In a typical synthesis, 7 nm spherical CeO$_2$ NCs (Fig. S1†) are dispersed in octadecene (ODE) and employed as seeds. A precursor solution containing copper acetate (Cu(OAc)) and the selected organic ligands (OLAM/OLAC, OLAM/OLAC/TOP or TOP only, where OLAM = oleylamine, OLAC = oleic acid, TOP = trioctylphosphine) in ODE is injected dropwise at 300 °C into the seed solution. OLAM and OLAC are common ligands in the synthesis of HNCs including one metal oxide domain, TOP was chosen as demonstrated to play an important role in the
formation mechanism of copper NCs. The dropwise injection was important to avoid homogeneous nucleation of copper. Various synthetic parameters (i.e. temperature, ligand concentration, amount of seeds) were optimized to maximize the yield of HNCs (i.e. 100 \times n^0 \text{HNCs}/(n^0 \text{isolated seeds} + n^0 \text{HNCs})).

**Structural characterization of the \((\text{Cu/CeO}_2)_n\) HNCs**

Fig. 1 gives an overview on the Cu/\(\text{CeO}_2\) HNCs synthesized with OLAC/OLAM (Fig. 1a and b), OLAM/OLAC/TOP (Fig. 1c and d) and TOP only (Fig. 1e and f). TEM images at lower magnifications are also provided in Fig. S2† to confirm the homogeneity of the samples. The HNC yield, as measured by statistical analysis in TEM images, was 80%, 92% and 90%, meaning that less than 20%, 8% and 10% of ceria seeds remain isolated, respectively. No homogeneously nucleated Cu NCs are identified. Representative X-ray diffraction (XRD) patterns of the HNCs are reported in Fig. S3.†

Transmission electron microscopy (TEM), high-angle annular dark-field scanning TEM (HAADF-STEM) and the relative area-selective energy-dispersive X-ray spectroscopy (EDXS) maps evidence the systematic formation of HNCs consisting of one central domain of spherical Cu, with an average size of around 15 nm, and one or more CeO\(_2\) domain seeds of around 7 nm. For the rest of the manuscript, these HNCs will be referred to as Cu/(\(\text{CeO}_2\))\(_n\) with \(n = 1,2,6\) indicating the average number of heterojunctions in each NC based on a statistical analysis of the stoichiometry distribution (Fig. 2). Concomitantly, elemental analysis performed by inductively coupled plasma-optical emission spectroscopy (ICP-OES) indicates decreasing Cu : Ce ratio as \(n\) increases (3.6 : 1, 2.1 : 1 and 1.7 : 1 for Cu/(\(\text{CeO}_2\))\(_1\), Cu/(\(\text{CeO}_2\))\(_2\) and Cu/(\(\text{CeO}_2\))\(_6\), respectively).

Investigation of the role of the ligands

Configurations of HNCs similar to Cu/(\(\text{CeO}_2\))\(_2\) and Cu/(\(\text{CeO}_2\))\(_6\) have been previously reported in the literature and were often referred to as flower- or clover-like structures. However, in these examples, the HNC core always consists of the NC seeds. Oppositely, in Cu/(\(\text{CeO}_2\))\(_2\) and Cu/(\(\text{CeO}_2\))\(_6\), the core is the nucleating Cu domain while the “petals” are the ceria seeds, which is both unique and surprising. As for the
mechanism, the formation of abovementioned flower- or clover-like structures has been correlated to the polarity of the solvent, the change of seed size or structure (single crystal vs. multi-twinned) and the reaction time. In our system, the solvent and the seeds are the same for all of the HNCs so their influence on the heterojunction formation can be ruled out. Instead, the chemical nature of the ligands clearly plays a significant role.

Ligands can impact NC nucleation and growth in two main ways: by modulating the surface chemistry and by acting as reactants in the synthesis (i.e. complexing agents or reductants). From the results above, it is clear that the presence of TOP in the reaction mixture induces the formation of multiple heterojunctions. Interestingly, no convincing evidence of the TOP acting as surface ligand on Cu/(CeO2)2 and Cu/(CeO2)6 HNCs was found by Fourier transform infrared spectroscopy (FT-IR) and XPS (Fig. S5†). Another possibility is that TOP alters the surface chemistry of the seeds by exchanging with the original OLAM ligand of the CeO2 NC seeds during the synthesis. However, no HNCs formed when TOP-coated CeO2 NCs were used as seeds in place of the OLAM-coated ones; instead, only homogeneous nucleation of Cu NCs occurred (Fig. S6†). These results suggest that TOP plays a key role as complexing agent for the formation of petal-like HNCs and must be involved in the Cu monomer formation as previously observed.31

Fig. 4 reports the NMR spectra of the precursor solutions (CuOAc + TOP) and (CuOAc + OLAM/OLAC). The data for the (CuOAc + TOP) mixture (Fig. 4a) indicate the formation of a [Cu(TOP)4][OAc] complex, where the acetate anion is non-coordinating. In the 31P{1H} NMR spectrum, the large shift of the free TOP signal to a more positive chemical shift, as well as the broadening of the resonance, are strong indicators of coordination to the Cu+ center.

All four coordinated TOP molecules are clearly symmetry equivalent, indicating a tetrahedral geometry. Likewise, in the 1H NMR spectrum, the free TOP alpha- and beta-CH2 resonances move to more positive chemical shift values after coordination to Cu+, and are also broadened due to the quadrupolar moment on Cu. A resonance for the OAc ligand was also observed, and its integration indicates the expected 1 : 4 ratio with TOP. No free TOP is observed in the precursor mixture.

In the case of the (CuOAc + OLAM/OLAC) mixture (Fig. 4b), there are a number of broad resonances in the 1H NMR spectrum that can be assigned to the 𝛼- and β-CH2 environments of either OLAM and/or OLAC. In a control experiment, OLAM and OLAC were mixed and the 1H NMR spectrum was measured; the spectrum was consistent with an oleylaminonium oleate salt, which forms from the acid-base reaction between OLAM and OLAC, as expected. The 1H NMR spectrum of the precursor mixture compared quite well with this spectrum, albeit with an important difference: the well-resolved resonances for the 𝛼-CH2 protons in the [OLAM-H][OLAC] salt (2.67 and 2.36 ppm) appear as a single broad resonance in the precursor mixture (2.44 ppm). An equivalent observation was made for the β-CH2 protons (peaks at 1.78 and 1.62 ppm averaging to 1.74 ppm). This loss of resolution could be due to association of the ammonium carboxylate ions with Cu+. The speciation of copper ions in ionic solutions has previously been shown to be quite complex, where transition metals tend to coordinate to additional anions, forming anionic complexes. These complexes are then surrounded by associated cations, in mono- or multinuclear aggregates. We therefore tentatively propose that Cu+ is coordinated by four oleyl ligands in a tetrahedral geometry, with three oleylaminonium counter ions balancing the charge, i.e. [Cu(OLAC)2][OLAM-H]3.

Discussion on the formation mechanism of the HNCs

Generally, two different mechanisms might take place to form the HNCs: an aggregative electrostatic self-assembly and heterogeneous nucleation. In the former, the Cu NCs would homogeneously self-nucleate in solution and successively assemble with the CeO2 seeds. Here, the ligands would modulate the surface passivation and charge to drive such a controlled attachment. In the heterogeneous nucleation, the CeO2 NCs would act as seeds for the nucleation of the Cu domain.

To get further insights, we monitored the temporal evolution for Cu/(CeO2)1 (Fig. S7†) and Cu/(CeO2)6 (Fig. 5). In both cases, the TEM analysis suggests that the configuration of the HNCs, with either single or multiple heterojunctions, is established since the early stages of the synthesis and an increased reaction time contributes towards the growth of the Cu domains (Fig. 5a–c). No evidence of homogeneously nucleated Cu NCs was found at any time. As for the CeO2 seeds, statistical analysis on the TEM images indicates a sudden drop of isolated NCs at around 75 s (Fig. 5d), which corresponds to the time at which the HNCs are first observed in the TEM images. In order to
exclude the impact of aggregation during drying of the TEM grid, dynamic light scattering (DLS) was performed as a complementary technique (Fig. 5e). Consistently with the TEM data, a continuous increase of particle size in solution is observed, which tracks well the increase in the Cu domain size. If aggregative growth of the HNCs occurred, a bimodal distribution should have been detected at some point, which was not the case. Therefore, as far as the current experimental evidences indicate, heterogeneous nucleation is the main mechanism behind the formation of the HNCs.

If heterogeneous seeded-growth is taking place, then the nature of the complexes formed between the ligands and the Cu precursor must play a role in determining the final configuration of the HNCs. Based on the metal–ligand bond strengths and on previous calculations, the copper–phosphine complex is expected to be more stable than the copper complex forming in the OLAM/OLAC mixture, and so to decompose more slowly and/or only at high temperature to release the copper monomer.

Overall, the absence of isolated Cu domains at any time during the synthesis along with no TOP on the surface of the HNCs and instead involved in the formation of Cu-TOP, suggest that electrostatic self-assembly is unlikely. While still speculative at this time, the ligand-regulated monomer saturation offers an alternative explanation to the undoubted role played by the ligands in determining the number of heterojunctions in the HNCs (Fig. 6).

**Impact of the number of heterojunctions on CO2 reduction reaction (CO2RR)**

To illustrate the importance of controlling the number of heterojunctions in the HNCs, the performance of the (Cu/CeO2)n hybrids as electro-catalysts for CO2RR were investigated. In a previous study, we found the Cu/CeO2 interface to promote CO2RR versus the competing hydrogen evolution reaction (HER) and to form methane as the major CO2RR product. Operando X-ray absorption spectroscopy (XAS) and DFT calculations explained this behavior based on the promotion of the Ce4+ → Ce3+ reduction and the concomitant formation of oxygen vacancies. The latter accounts for improved stabilization of the key CO2RR intermediates [CHO* and H2CO*] at the Cu/CeO2 interface. Based on these results, understanding if an increased interfacial area further enhances these beneficial effects is interesting and crucial to develop better catalysts.

Fig. 7a reports the faradaic efficiencies (FE) and CO2RR partial current densities (j_CO2RR) normalized by the electrochemically active surface area (ECSA) for Cu-CeO2 physical mixture, Cu/(CeO2)1, Cu/(CeO2)2, and Cu/(CeO2)6.
Among the CO$_2$RR products, both ethylene and methane are reference. First of all, the results evidence that the Cu/(CeO$_2$)$_1$ heterojunction increases, the CO$_2$RR FE decreases to around 37% and 32% for Cu/(CeO$_2$)$_2$ and Cu/(CeO$_2$)$_6$, respectively.

HNCs, respectively. Data for isolated Cu and CeO$_2$ NCs of similar sizes of the HNC domains are reported in Fig. S11† for reference. First of all, the results evidence that the Cu/(CeO$_2$)$_3$ HNCs outperform the isolated Cu NCs and Cu–CeO$_2$ physical mixture in terms of total FE towards CO$_2$RR, which reaches up to 60%. The higher $J_{\text{CO2RR}}$ indicates that such increase in FE is related to the higher intrinsic activity of the HNCs. In agreement with our previous study, Cu/(CeO$_2$)$_3$ produce methane as the major product with FE up to 50%. This result highlights the role of the hetero-junction obtained by employing the colloidal synthesis method presented herein. Notably, as the number of heterojunctions increases, the CO$_2$RR FE decreases to around 37% and 32% for Cu/(CeO$_2$)$_2$ and Cu/(CeO$_2$)$_6$, respectively. Among the CO$_2$RR products, both ethylene and methane are suppressed while CO and formate are promoted. Concomitantly, the $J_{\text{CO2RR}}$ is lower for the two samples compared to the single junction HNCs. Overall the FE$s$ for CO$_2$RR of Cu/(CeO$_2$)$_{n=2}$ HNCs are comparable to the isolated Cu NCs (Fig. S11†), however the ratio of C$_2$/C$_3$ products is increased which could be an indication of interrupted pathway toward C$_2$ products. The lower $J_{\text{CO2RR}}$ indicates that the overall intrinsic activity towards CO$_2$RR decreases as well.

To gain further insight into the oxidation states of the Cu and Ce domains during CO$_2$RR, we performed operando XAS measurements. Fig. 7b shows the concentration profiles of Ce$^{4+}$ (solid symbols) and Ce$^{3+}$ (open symbols) as a function of the reaction time at the operating potential. These values were extracted from a time-resolved map via multivariate spectral analysis (Fig. S12†). In all three samples, we observed the reduction Ce$^{4+} \rightarrow$ Ce$^{3+}$ over time until reaching a steady state value. Instead, the Cu counterpart, partially oxidized at the beginning of the experiment, reduced very quickly and at a similar rate in all the samples as soon as the negative operating potential was applied; then, it remained stable in its metallic form during the catalysis (Fig. S12†). Importantly, we found that a larger fraction of Ce$^{3+}$ forms in the Cu/(CeO$_2$)$_1$ HNCs compared to the Cu/(CeO$_2$)$_{n=2}$ HNCs (roughly 25% > 15% > 10% as $n$ increases from 1 to 6). Thus, the results from the operando XAS of Ce L$_3$-edge confirm the positive correlation between Ce$^{3+}$ and the CO$_2$RR promotion. They also suggest that the presence of multiple metal oxides surrounding the Cu NCs inhibits the Ce$^{4+} \rightarrow$ Ce$^{3+}$ transformation, which is opposite to what expected based on increased interfacial area. One possible explanation is that, as the number of heterojunctions increases, the constant number of the charges (supplied from applied negative potential, $-1.2$ V$\text{RHE}$) have to be distributed among a higher number of ceria NCs. As the loading and size of the Cu NCs in all the samples are constant, it’s reasonable that the charge portion allotted to each ceria NCs would decrease.

Moreover, one must consider that increasing the number of ceria domains reduces the copper surface available to perform CO$_2$RR. The CeO$_2$ NCs themselves are mostly active for HER (Fig. S11†), therefore we hypothesize that the increased HER results from their increase weight fraction in the catalyst. As the protons are consumed by the ceria, less remain available for the proton coupling steps needed to convert CO to higher hydrocarbons. Thus, mostly CO increases among the CO$_2$RR products while CH$_4$ and C$_2$H$_4$ decrease. More detailed studies are planned for the future to further corroborate this hypothesis. For example, HNCs with a reverse configuration where the several Cu NCs nucleated on one CeO$_2$ seed, would be an interesting system to study as the number of heterojunctions will increase without compromising the Cu surface available for the CO$_2$RR to take place.

**Generality of the synthetic method**

Finally, having learned the crucial role of the organic ligands in controlling the number of heterojunctions in the Cu/CeO$_2$ HNCs, we decided to investigate if the same synthesis approach could be applied to different systems. We selected ZrO$_2$ and ZnO as examples, because Cu/ZrO$_2$ and Cu/ZnO interfaces are of potential interest for both CO$_2$ hydrogenation and CO$_2$RR.† Fig. 8 depicts the Cu/ZnO (Fig. 8a–c) and Cu/ZrO$_2$ (Fig. 8d–f) HNCs that were successfully obtained with a configuration resembling that of Cu/CeO$_2$, where the central copper domain is decorated by a number of metal oxide seeds, and with the number of heterojunctions increasing as OLAM/OLAC, OLAM/OLAC/TOP or TOP only were used as the organic ligands.

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**Fig. 7** CO$_2$RR performance of the Cu/(CeO$_2$)$_n$ HNCs. (a) Faradaic efficiencies and CO$_2$RR partial current-densities for Cu/(CeO$_2$)$_1$, Cu/(CeO$_2$)$_2$ and Cu/(CeO$_2$)$_6$ and Cu–CeO$_2$ physical mixture measured at $-1.2$ V$\text{RHE}$ in 0.1 M KHCO$_3$. It is worth mentioning that the total FE of the samples are less than 90%. Oxidation of some unaccounted formate and methanol at the platinum anode has been reported to contribute to the lack of 100% total FE. Also, some electrons may be used for the formation of oxygen vacancies in CeO$_2$–Ce, thus, contributing to non-productive current. (b) Concentration profiles of Ce$^{4+}$ (solid symbols) and Ce$^{3+}$ (open symbols) derived from the multivariate analysis of Ce L$_3$-edge XANES spectra during CO$_2$RR.

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**Fig. 8** CO$_2$RR performance of the Cu/ZnO (Fig. 8a–c) and Cu/ZrO$_2$ (Fig. 8d–f) HNCs. The Cu/ZnO NCs themselves are mostly active for HER (Fig. S11†), therefore we hypothesize that the increased HER results from their increase weight fraction in the catalyst. As the protons are consumed by the ceria, less remain available for the proton coupling steps needed to convert CO to higher hydrocarbons. Thus, mostly CO increases among the CO$_2$RR products while CH$_4$ and C$_2$H$_4$ decrease. More detailed studies are planned for the future to further corroborate this hypothesis. For example, HNCs with a reverse configuration where the several Cu NCs nucleated on one CeO$_2$ seed, would be an interesting system to study as the number of heterojunctions will increase without compromising the Cu surface available for the CO$_2$RR to take place.
during the synthesis. While some system specific differences emerge in the final HNCs (i.e. the faceted morphology of the Cu domain in Fig. 8d, which might stem from some effects induced by the crystallinity of ZrO\(_2\) seeds\(^{3,6,16,17,22–25,33,34}\)), the results suggest that the method is indeed general.

Conclusions

In summary, we have successfully developed a seeded-growth approach to synthesize Cu/metal oxide HNCs with adjustable numbers of interfaces. Investigating the role of the ligands was key to understand that they affect the copper precursor stability and, thus, the monomer saturation, which in turn governs the growth regime and the final configuration of the HNCs. Finally, we also demonstrate that the achieved degree of architectural tunability is crucial to explore synergistic interface effects in catalysis. By testing Cu/(CeO\(_2\))\(_n\) as electrocatalysts for CO\(_2\)RR, we learned that optimal electrocatalytic properties are obtained as a trade-off between interfacial synergy and geometric configuration determining accessibility of the catalytic surfaces.

Having tunable materials platforms, like the (Cu/CeO\(_2\))\(_n\) HNCs reported in this study, becomes crucial to enable these correlations in catalysis and in other applications where these interfaces might be useful, such as plasmonic, biomedical, sensing and photocatalysis applications\(^{5,11,12,25–37}\). Therefore, additional efforts in the community to understand the chemistry behind the formation of such tailored structures are important to further master the synthesis of other non-noble metal/metal oxide HNCs.

Experimental section

Chemicals

Copper(i) acetate (or CuOAc, 97%), trioctylphosphine (\([\text{CH}_3\text{CH}_2]_3\text{P}\), or TOP, 90%), oleic acid (C\(_{17}\)H\(_{33}\)CO\(_2\)H or OLAC, 90%), oleylamine (C\(_{17}\)H\(_{33}\)NH\(_2\) or OLAM, 70%), 1-octadecene (C\(_{18}\)H\(_{36}\) or ODE, 90%) were all purchased from Sigma-Aldrich and used as received.

Synthesis

**Synthesis of Cu/(MO\(_2\))\(_n\) HNCs (M = Ce, Zn, Zr).** As a general procedure, 30 mL of the ODE solution containing the MO\(_2\) seeds (0.5 mM) in a 100 mL three-necked flask were degassed under dynamic vacuum for 20 min at 130 °C, after which they were heated under N\(_2\) flow to 300 °C for 5 minutes. A precursor solution was prepared by mixing 0.1 mmol CuOAc and 0.4 mmol of OLAM/OLAC in degassed ODE (1.4 mL). 450 μL of this solution were then added dropwise to the flask containing the seeds at a rate of 0.18 mL min\(^{-1}\) using a syringe pump, meanwhile the reaction mixture slowly turned from colorless to
brown. At the end of the injection, after around 150 s, the reaction was stopped and the mixture was allowed to cool down to room temperature by removing the heating mantle. The HNCs were extracted and purified by repeated washing/centrifugation cycles inside a N₂ glovebox to avoid Cu oxidation. 30 mL each of anhydrous ethanol and toluene were added to the reaction mixture at room temperature and the mixture was divided into 4 centrifugation vials; the particles were collected by centrifugation at 5000 rpm for 15 min. The precipitate was washed twice with ethanol to remove unreacted precursor and surfactants. Finally, the HNCs were re-dispersed in hexane or toluene.

**Synthesis of Cu/(MO₃)₆ HNCs (M = Ce, Zn, Zr).** The same procedure was used as for the synthesis of Cu/(MO₃)₆ HNCs except the precursor solution contained 0.1 mmol of CuOAc, 0.396 mmol of TOP, 0.02 mmol of OLAM and 0.02 mmol of OLAC.

**Characterization**

**Electron microscopy.** Samples were drop-cast on a copper TEM grid (Ted Pella, Inc.) prior to imaging. BF-TEM images were taken with a FEI Tecnai Spirit at 120 kV. HAADF-STEM imaging and energy dispersive X-ray analysis (EDX) were performed on a FEI Tecnai Osiris transmission electron microscope in scanning mode at an accelerating voltage of 200 kV. This microscope is equipped with a high brightness X-FEG gun, silicon drift Super-X EDX detectors and a Bruker Esprit acquisition software. Aberration-corrected (Cs) high-resolution S/TEM imaging were performed on a FEI Titan Themis 60–300 at an accelerating voltage of 200 kV.

**Nuclear magnetic resonance (NMR).** All NMR spectra were recorded on a Bruker AVANCE III HD 400 spectrometer fitted with a 5 mm BBFOz probe, operating at 400.13 MHz for ¹H NMR spectra and 161.98 MHz for ³¹P{¹H} NMR spectra. ¹H NMR chemical shifts were referenced internally to residual solvent resonances (d₆-benzene, δ_H = 7.16 ppm; d₆-toluene, δ_H = 7.09 ppm), calibrated against an external standard (SiMe₄, where δ_H = 0 ppm).

**Dynamic light scattering (DLS).** DLS spectra were collected on a Brookhaven Zeta instrument. Aliquots were extracted from the reaction mixture at different times and diluted in toluene. The DLS cell was sealed under N₂ or ambient atmosphere during the whole test period.

**Inductively coupled plasma-optical emission spectrometry (ICP-OES).** ICP-OES was performed on Agilent 5100 model to determine the Ce and Cu concentration in Cu/CeO₂ NCs, Cu-CeO₂ physical mixture and individual Cu NCs. For the digestion of the solutions, upon evaporation of the hexane, 280 μL of each HNO₃ (70%) and H₂O₂ (35%) was added to 100 μL of the as-synthesized NCS solutions and left overnight to ensure complete digestion of the samples. Following this step, 9.5 mL of Milli-Q water was added to the solution to reach the 2% acid content needed for the analysis. 5 standard solutions of Ce and Cu were prepared to obtain the calibration curve that was used to determine the concentrations of the digested solutions.

**Electrocatalytic measurements**

**Electrode preparation.** Glassy-carbon plate electrodes (Type 2, Alfa Aesar, 2.5 cm × 2.5 cm) were used as substrates. They were polished using Milli-Q water slurries of 1 μm diamond (Bioanalytical Systems, Inc.) and 50 nm gamma alumina (Bioanalytical Systems, Inc.) on polishing pads. The plates were rinsed with Milli-Q water, sonicated in Milli-Q water for 10 minutes, and blown dry with nitrogen. The NCs were drop-casted on the substrate from their toluene suspension with a Cu mass loading of 15 μg for all the samples.

**Electrocatalytic measurements.** The electrocatalytic measurements were performed in a conventional H-cell, used in previous work by our group and by others.⁹ A Biologic SP-300 was used as the potentiostat. Platinum foil was employed as the counter electrode and an Ag/AgCl reference electrode (leak free series from Innovative Instruments, Inc.) was used. Voltages were converted to the reversible hydrogen electrode (RHE) scale.

For gas product analysis, a gas chromatograph (GC, SRI instruments) equipped with a HayeSep D porous polymer column, thermal conductivity detector, and flame ionization detector was used. Ultrahigh purity N₂ (99.999%) was used as a carrier gas. After passing through the cell, CO₂ was flowed directly into the gas-sampling loop of the GC for online gaseous product analysis, which was carried out every 10 min. For all experiments, electrolysis was carried out for 80 min with gas analysis recorded at 10 min intervals. The liquid products were collected from the electrolyte after electrolysis and analyzed by the high-performance liquid chromatography (HPLC) on an UltiMate 3000 instrument from Thermo Scientific.

**Operando X-ray absorption spectroscopy (XAS)**

Operando XAS experiments were performed at the SuperXAS beamline at the Swiss Light Source synchrotron facility (Paul Scherrer Institute, Switzerland). The measurements were performed in fluorescence mode at an incident angle of about 45 degrees.

We employed a dedicated set-up for the low energy Ce L₃-edge as described in our previous work.⁹ The catalyst solution was drop-casted on a thin (2.5 × 2.5 × 0.5 mm³) glassy carbon (GC) support and a Kapton window allows the X-rays to pass through. Additional details for the data analysis are reported in the ESL.¹

**Conflicts of interest**

There are no conflicts to declare.

**Acknowledgements**

This work was primarily financed by the European Research Council under Starting Grant ERC-HYCAT with agreement on DLS. The work was also supported by the Chemistry Department of the Technion Institute of Technology. The authors gratefully acknowledge the Swiss National Science Foundation for the funding of the project "SOLO: Solubility and Optimal Loading of Oxide Catalysts" (project number 200021-185751).
number 715634. D. S. is supported by the Sandoz foundation. The authors thank Dr Mounir Mensi for the acquisition of the XPS data and Ona Segura Lecina for her contribution to NMR spectroscopy. The authors acknowledge the Paul Scherrer Institut, Villigen, Switzerland for provision of synchrotron radiation beamtime at beamline SuperXAS of the SLS and would like to thank Dr Adam Clark for assistance.

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