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# Well performing Fe-$SnO_2$ for $CO_2$ reduction to HCOOH

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ABSTRACT

The climate change imposes to mankind a severe management of $CO_2$ emissions in atmosphere. $CO_2$ valorization through electrocatalysis revealed to be a valuable solution to this global issue. $SnO_2$ is an electrocatalyst widely investigated for its capability to reduce $CO_2$ to formic acid. In particular, mesoporous $SnO_2$ offers a high adsorption capability, resulting in a high catalytic activity. In order to improve its performance, Fe-doping is here investigated for the first time. We observed that Fe-doped $SnO_2$ exhibits a remarkable 100% enhancement of the partial current density for HCOOH production at relatively low overpotentials, although keeping the selectivity unchanged.

## 1. Introduction

According to the Paris agreement, the control of climate change imposes a common effort among all the nations through the control and limitation of $CO_2$ emissions in atmosphere. In order to reach this goal, different strategies have been adopted. [1–3] Among them, catalytic $CO_2$ reduction reaction ($CO_2$RR) is the more valuable since it allows to convert $CO_2$ into a resource, namely a carbon-based fuel or a chemical.

Aiming to obtain a novel, well-performing, cheap and easily scalable catalyst, the attention has been focused on tin oxide ($SnO_2$) and its doped forms. Tin oxide is an attractive semiconductive material with high catalytic power and non-noble, eco-friendly and low-cost characteristics. [4] From the catalytic point of view, $SnO_2$ is particularly interesting because of its a high selectivity to formic acid (HCOOH). [5] From the perspective of a large-scale application of the catalyst, the selectivity would ease the $CO_2$RR product separation: the liquid HCOOH from the gaseous minor products (CO and $H_2$).

A great number of methods have been developed until now to prepare nanostructured $SnO_2$ catalysts [6–8] Among them, anodic-oxidation (AO) of tin foils unveiled to be a simple, high yield, low-cost, scalable, easily reproducible and effective strategy to prepare nanostructured porous materials. [9] As already demonstrated by Bejtka et al., [10] sponge-like $SnO_2$ realized via AO is capable to reduce $CO_2$ to formic acid with good selectivity.

The main chasing properties of a performing electrocatalyst are (i) the good selectivity through products, (ii) the low energy requirements, i.e. the lower the reaction over-potential the better, and (iii) the high electron transfer, which stands for high current densities at low bias. The applied potential for $SnO_2$-based catalysits is commonly more negative than −1 V vs Reversible Hydrogen Electrode (RHE). Only few works are reported in literature with a lower overpotential (around −0.8 V vs RHE). As an example, Kumar et al. [7] realized $SnO_2$ nanoparticles capable to reduce $CO_2$ to HCOOH at −0.8 V vs RHE, although with a partial current of just −1.4 mA/cm$^2$. A similar result was obtained by the same group with porous nanowalls, [7] and by Ge et al. [11] with mesoporous structures. In order to reach higher partial currents, the potential has to be more negative. Partial current denisties over −10 mA/cm$^2$ were reached with Sn dendrite [12] and chainlike mesoporous $SnO_2$, [10] but with applied potentials lower than −1.1 V vs RHE.

To overcome these limitations, doping has been investigated [13,14] as a possible way to induce nanostructure modification, together with the density of states engineering to push the catalytic properties of $SnO_2$ toward $CO_2$ reduction at lower overpotentials.

As proved by literature, in systems containing metals, like Au and Cu, the broken spatial symmetry near grain boundaries changes the binding energy of the reaction intermediates, facilitating the $CO_2$ reduction to CO [15] and its reduction to $C_{2+}$ products, [16] thus arousing the attention in the study of modified-$SnO_2$. The effect of doping results in an upward shift in the Pourbaix diagram boundary separating the [3H/1$CO_2$] and [4H/1$CO_2$] states. This means that dopants should lower the

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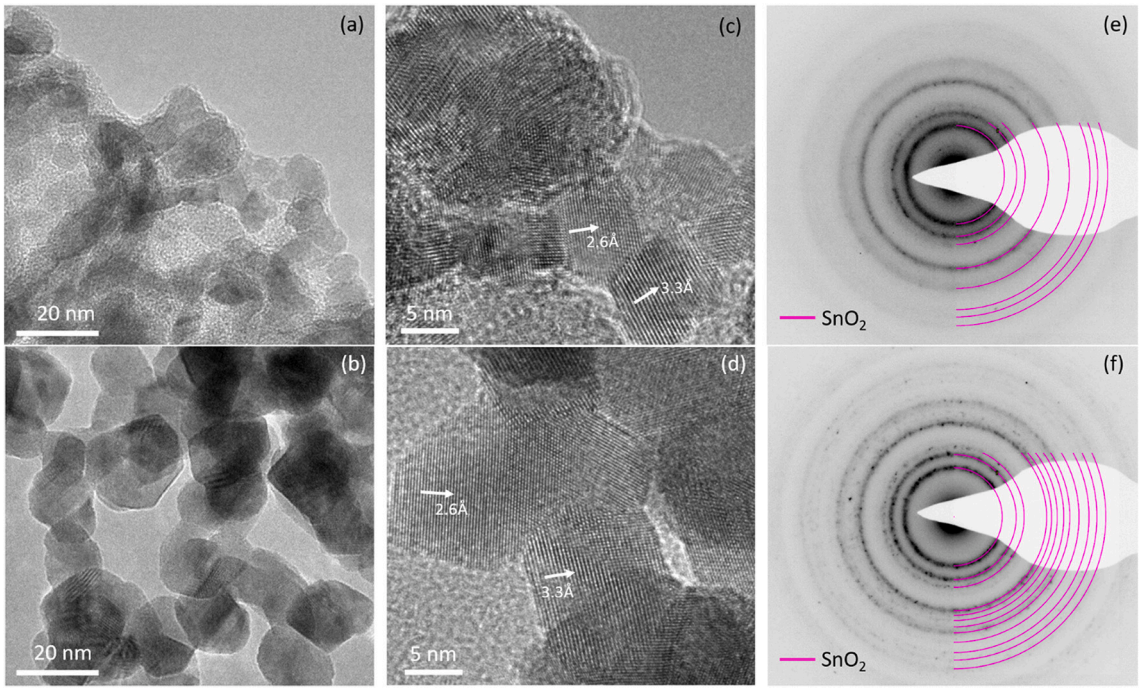



**Fig. 1.** TEM characterization: BF-TEM (a, b) HR-TEM (c, d) and SAED (e, f) for $SnO_2$ (a, c, e) and Fe-$SnO_2$ (b, d, f) respectively. In HR-TEM images interplanar spacings calculated from FFT (not shown) are provided (~3.3 Å (110), ~2.6 Å (101) family of planes of the $SnO_2$ structure). In SAED images a simulated pattern for $SnO_2$ crystal structure is also shown.

over-potential for $CO_2$ reduction with respect to un-doped tin oxide. For this reason, doping has been suggested by Saravanan et al. [14] as good strategy for future experimental investigations on energetically efficient $CO_2$ reduction.

We selected Fe-doping because the inclusion of $Fe^{3+}$ ion is expected to induce a p-type behaviour in $SnO_2$, thus increasing the resistivity of the material [20–22], and to introduce oxygen vacancies [22,23] which are beneficial for $CO_2$RR. Albeit Fe-doped $SnO_2$ has been already investigated for different applications, [17–23] to the best of our knowledge it has never been studied as electrocatalyst for $CO_2$RR.

$SnO_2$ was synthesized via AO, following the procedure presented by Bejtka et al. [10]. The doping has been attained following the procedure developed by Jain et al. [24] on Ni-doped $SnO_2$ (synthesis reported in the SI). The same dopant molar concentration and synthesis parameters were kept in order to establish a starting procedure. A complete structural characterization has been carried on. Fe-doped $SnO_2$ has been then tested as electrocatalyst for $CO_2$RR. As a result, the material exhibits a good selectivity toward formic acid (HCOOH) with a secondary production of CO and $H_2$. The selectivity toward HCOOH and CO is taken as a great advantage since they are easily separable; moreover, CO and $H_2$ can be employed to obtain syngas. [25]

## 2. Results and discussion

### 2.1. Material characterization

The un-doped $SnO_2$ samples annealed at 600 °C display a porous and irregular structure (Fig. S1 a–b), composed by nanochannels, with about 50 nm mean diameter and wall thickness of about 15 nm, which is typical for $SnO_2$ prepared by anodic oxidation. [10] The TEM characterization shown in Fig. 1 a and c gives more detailed information on morphological and structural properties. The bright field (BF) and HR-TEM show that the pore walls are made of small-interconnected crystals, with a size in the range of 5–20 nm. The ring pattern in Selected Area Electron Diffraction (SAED), analyzed with the Circular Hough analysis tool [26] of Digital Micrograph™ software, confirms the polycrystalline nature of the sample, and the crystalline phase present of $SnO_2$ (tin oxide, JCPDS 00–041-1445).

The mesoporous structure, created during the synthetic process, allow the easy access of the electrolyte to the catalytic sites and efficient mass diffusion. [11] Moreover, the nanostructuration with tailored surface configuration proved to be an effective strategy to enhance the catalytic activity. [15,16]

Vertically aligned nanochannels were observed in $SnO_2$ realized by anodic oxidation by the group of Palacios-Padròs [27] and in our previous work, [10] with fully open pores, whose diameter is compatible with the one we measured. This implies that the increase of the annealing temperature to 600 °C (necessary for the doping step) does not affect the sample morphology.

The introduction of Fe doping into $SnO_2$ sample leads to the formation of bigger crystals, with good crystallinity (Fig. 1e), clearly discernible in the FESEM (Fig. S1 c) and BF-TEM (Fig. 1d) images. The increased crystal-size, which, on the basis of HR-TEM images, is of about 12–35 nm, causes the closure of the channels, which are no more discernible in the top-view FESEM image (Fig. S1 c). The structural characterization by SAED shows the ring pattern with reflections from numerous $SnO_2$ planes (tin oxide, JCPDS 00–041-1445), with no significant distortion to the unit cell. Although there is no detectable evidence of the dopant in the diffraction pattern, the EDX analysis confirms the presence of Fe in the doped-$SnO_2$ powder samples, as shown in Fig. S2. The lack of any evidence of the presence of metal clusters neither in HR-TEM nor in SAED suggests the dopants are well spread and completely inserted in the $SnO_2$ lattice.

A further investigation of the crystalline structure of the $SnO_2$ samples was carried out with XRD in Bragg-Brentano configuration. The obtained patterns correspond to $SnO_2$ (JCPDS 00–041-1445) with no significant variations of peak positions among the doped and un-doped samples (Fig.S3). The peak shape and FWHM in the un-doped sample give evidence of small coherent diffraction domains in this sample. Narrower peaks observed in Fe-$SnO_2$, which according to the Scherrer equation, give the evidence of increased size of coherent diffraction domains with respect to the un-doped sample, and this is consistent with

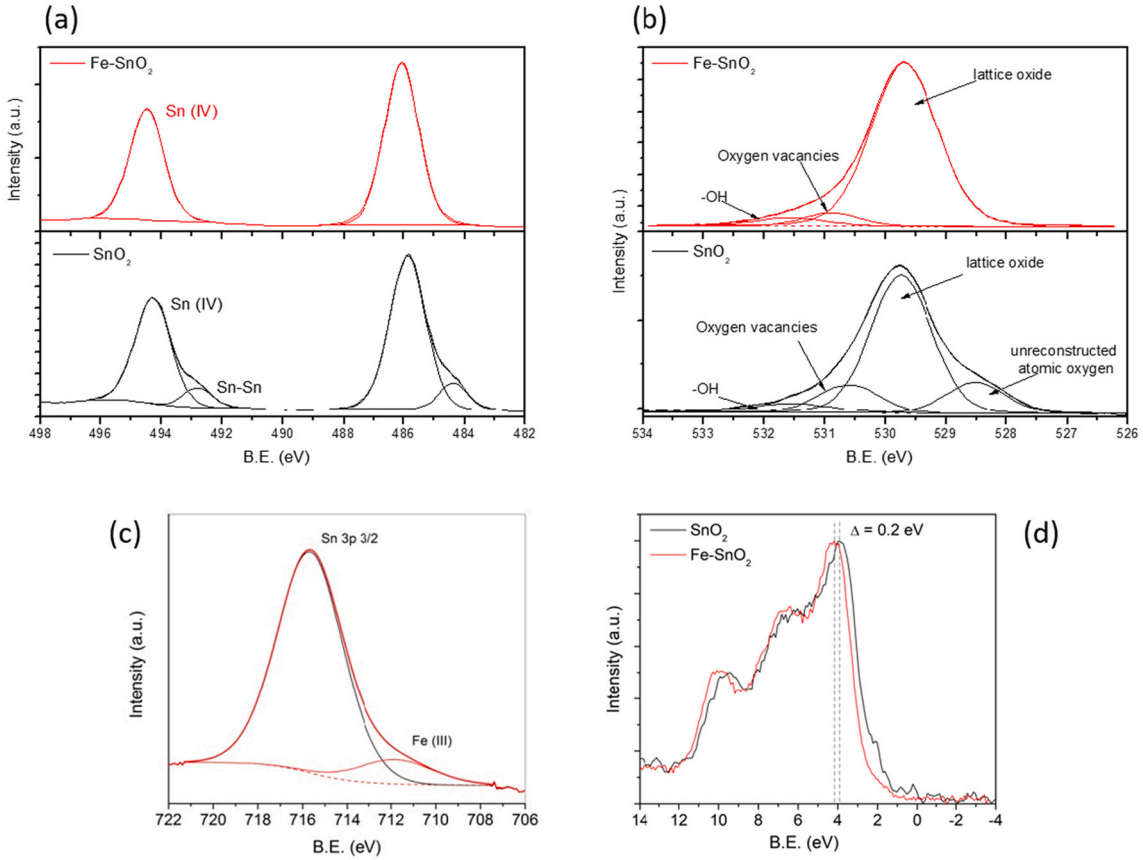



**Fig. 2.** XPS spectra of Sn 3d and O 1 s orbitals of SnO2 (a) and Fe-$SnO_2$ (b) respectively. Fe 2p of Fe-$SnO_2$ sample (c) and valence band spectra (d) are also shown. For sake of clarity, the spectra referred to $SnO_2$ are black, while the ones related to Fe-$SnO_2$ are red. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

the TEM observation. The result is also in good agreement with the outcomes of Kaur et al. who found that Fe incorporation in $SnO_2$ lattice resulted in increasing grains size. [28]

Concerning the surface chemical composition, $SnO_2$ samples were characterized with XPS, using C 1 s peak (284.5 eV) to calibrate the spectra.

The survey spectra are reported in Fig. S4; Sn and O were observed in both samples, with small traces of adventitious carbon. Fe has been observed in the Fe-$SnO_2$ samples, which is consistent with the EDX results.

The Sn 3d doublet of $SnO_2$ sample is located at 485.9 eV (Sn $3d_{5/2}$) and 494.3 eV (Sn $3d_{3/2}$) as shown in Fig. 2 a. Since the peaks due to Sn (II) and Sn (IV) are close to each other, it is not trivial to distinguish the oxidation state of the compound. For this reason, the valence band (VB) shape has been used for the identification: as shown in Fig 2 d, the VB region displays the typical $SnO_2$ three-peaked structure. [29] Thus the most abundant oxidation state results to be Sn (IV), as also suggested by the 8.4 eV peaks distance related to the spin-orbit split. [10]

The small shoulders at lower binding energy (484.4 eV and 492.8 eV) can be ascribed to Sn—Sn, as reported by R. Shiratsuchi et al. [30]

The O 1 s spectrum (Fig. 2 b) confirms the presence of lattice oxide, displaying a strong component located at 529.7 eV, a small contribution due to O surface vacancies at 530.6 eV and a smaller component due to –OH species, as defined by the component at 531.5 eV. [31] A further peak located at 528.5 eV can be ascribed to unreconstructed atomic Oxygen, as reported by T.E. Jones et al. [32]

As regard Fe-$SnO_2$, the shift due to Sn—Sn bond in Sn3d doublet (see Fig. 2 a) and the peak due to O1s lowest chemical shift at 528.5 eV (Fig. 2 b) are disappeared. For both samples the presence of the Oxygen vacancy related peak is of fundamental importance since for application in $CO_2$ valorisation, oxygen vacancies are believed to participate in the catalysis by enhancing $CO_2$ adsorption and, as a consequence, its reduction.

As regard the dopant (Fig. 2 c), the peak maximum of Fe $2p_{3/2}$ stands at 711.7 eV. The position is connected to the oxidation state of Fe (III), [33] thus suggesting that iron was successfully inserted in the oxide structure. The close peak, located at 715.5 eV is referred to Sn $3p_{3/2}$, which is partially overlapping the Fe 2p doublet, as also observed by Xing et al. [34]

By looking at the VB region (Fig. 2 d), a 0.2 eV shift at higher binding energies has been observed for Fe-$SnO_2$. A similar outcome has been already published in literature by Egdell et al. [35] in their study concerning Sb-doped $SnO_2$ materials. In their findings the experimental results were explained by the presence of segregated doping atoms at the surface, a phenomenon which induces a shrinkage in the energy gap and a subsequent shift toward higher binding energies of the VB onset, thus proving the doping achievement.

### 2.2. *Electrochemical and $CO_2$ reduction tests*

Prior to $CO_2$RR test, CV has been carried out to first check the performances of the doped and un-doped samples. The CV plot in Fig. S5 shows that with equal potential, Fe-$SnO_2$ exhibits a higher current than $SnO_2$, which means that the Fe-doped electrodes have higher activity (higher geometric current).

The doped and un-doped $SnO_2$ samples have been, then, tested for $CO_2$RR in the same potential range (from −0.69 to −0.89 V vs RHE), and the production of formic acid has been analyzed.

As a result, the un-doped $SnO_2$ exhibits a maximum of HCOOH production, 40.0% of Faradaic efficiency (FE, eq. S1), at −0.89 V vs RHE

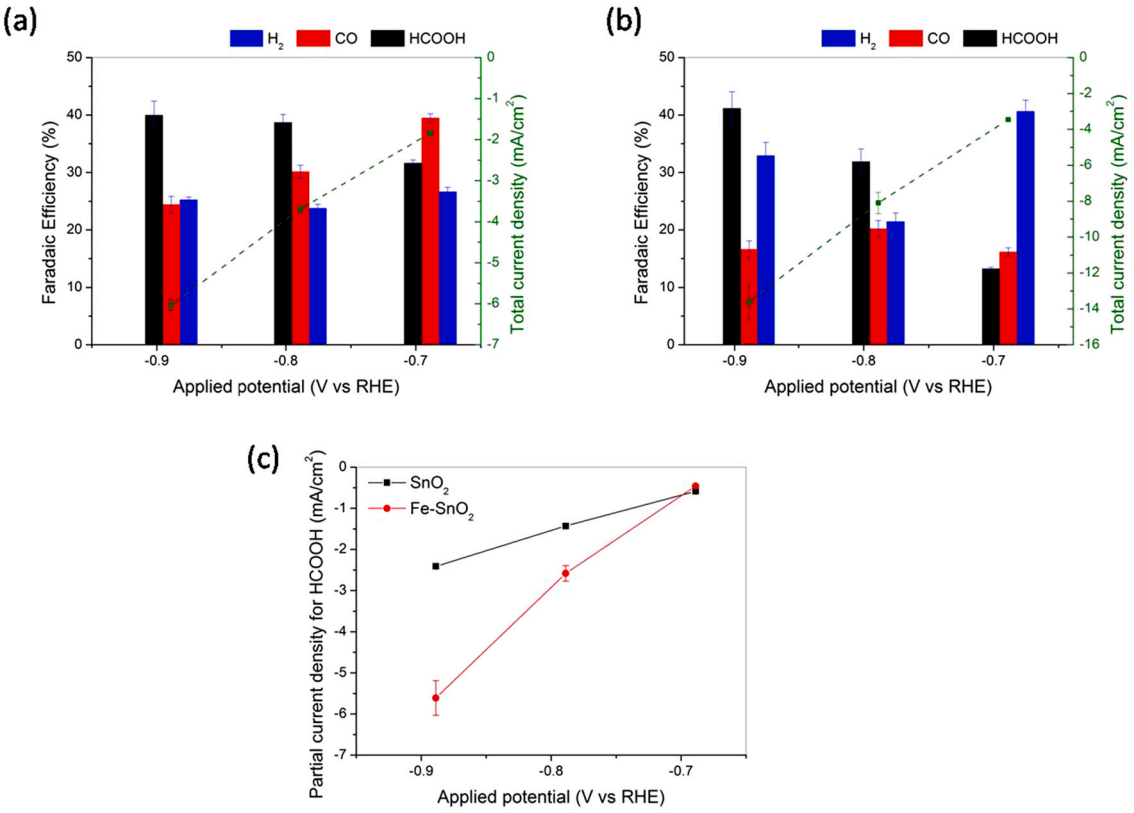



**Fig. 3.** Bar chart representing the Faradaic efficiencies for $SnO_2$ (a) and Fe-$SnO_2$ (b) for each tested potential. In green, the current density curve shows the behaviour at different applied potentials. (c) Partial current densities related to HCOOH production. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

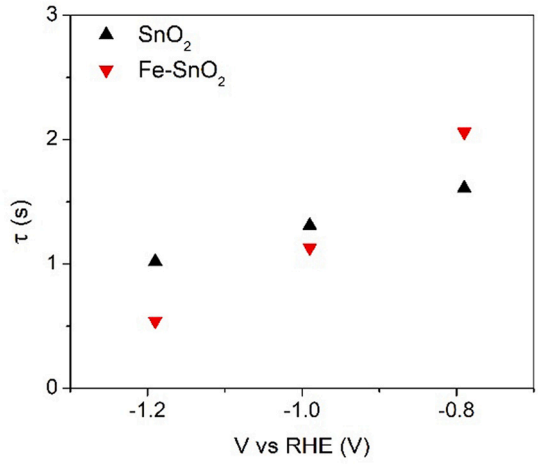



**Fig. 4.** Charge transfer time calculated for $SnO_2$ and Fe-$SnO_2$.

with a secondary production of $H_2$ and CO (Fig. 3 a). A stable total current density of $-6.0$ mA/cm$^2$ is obtained during 1 h of $CO_2$ reduction as shown in Fig. S6. The resulting FE is compatible to the one reported by Ge et al. [11] on mesoporous $SnO_2$, albeit with lower current densities. Moreover, the FE for HCOOH production is lower with respect to our previous work on $SnO_2$ electrocatalyst calcined at 450 °C; [10] however, it is woth notice that the over-potential corresponding to maximum HCOOH production has been lowered in the present work.

Similarly, Fe-$SnO_2$ exhibits the maximum of HCOOH production at the same potential ($-0.89$ V vs RHE) with a FE of 41% (Fig. 3 b). At this potential, $CO_2$ is reduced mainly to HCOOH, with $H_2$ and CO as secondary products. It is worth noting that the total current density of Fe-$SnO_2$ is more than two times higher than $SnO_2$, with a value at the equilibrium of $-14$ mA/cm$^2$. Thus, keeping the same selectivity of bare $SnO_2$, it is possible to double the efficiency of $CO_2$ reduction, as evident from the HCOOH partial current densities calculated trough eq. S2 (Fig. 3 c), to easily separable products. As expected, while the applied potential negatively increases, the equilibrium of the reaction moves from $CO_2$ reduction to $H_2$ evolution: for this reason, potentials more negative than $-0.89$ V vs RHE have not been investigated (further discussion on the reaction mechanism in the Supporting Information). The low overpotential makes the sample particularly interesting, especially for its relatively high current. The obtained high activity for HCOOH production (5.44 mA/cm$^2$) results to be among the highest ever reported for tin-oxide based electrocatalysts at potentials higher than $-1$ V vs RHE, as reported in Table S1.

The performance of Fe-$SnO_2$ has been investigated via EIS. By analyzing the impedance of both the samples (Fig. S7), a different behaviour of the charge transfer kinetics has been observed at the catalyst/electrolyte interface. In fact, by looking at the transfer time (Fig. 4), it is possible to observe a faster kinetic for Fe-$SnO_2$ with respect to bare $SnO_2$ while the potential is increasing. This imply that, in the former catalyst, a larger number of charges is available at the surface for the reduction reactions.

This result confirm that Fe-doping is an effective strategy in improving the performance of $SnO_2$ catalyst for $CO_2$RR.

## 3. Conclusion

A cheap and easily scalable technique to fabricate Fe-doped $SnO_2$ has been presented. The material has been tested for the first time for $CO_2$RR and demonstrated to be a valuable electrocatalyst for HCOOH

production. The highly porous structure, observed with FESEM, offers a high concentration of catalytic centres per unit area. Moreover, the presence of Fe-doping, confirmed by XPS analysis, demonstrated to be capable to keep the same selectivity of $SnO_2$, but increasing the production rate. In fact, a 100% enhancement of current density was observed at a relatively low potential of −0.89 V. The analysis of the impedance through EIS allowed to explain the result showing a faster charge transfer of Fe-$SnO_2$ sample with respect to $SnO_2$. In order to complete the investigation on the catalyst, stability tests will be carried out and the results will be presented in a future broader publication.

Although a further optimization of the catalyst is still possible, nevertheless, Fe-doped $SnO_2$ demonstrates to be a promising material for future technologies for $CO_2$RR.

## Data availability

The data are available by contacting the corresponding author.

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Conceptualization and synthesis of the materials. Electrochemical measurements, gas-products measurement, data analysis and interpretation.

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EIS data analysis and interpretation.

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Undoped-catalyst conceptualization. Electron microscopy measurements (SEM and TEM), EDX measurements, data analysis and interpretation.

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XPS measurements, data analysis and interpretation.

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First author's supervisor.

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## Declaration of Competing Interest

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.

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## Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.catcom.2022.106412.

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