Synergy or Antagonism? Exploring the Interplay of SnO_2 and an N-OMC Carbon Capture Medium for the Electrochemical CO_2 Reduction Towards Formate

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Abstract

Closing the anthropogenic carbon cycle by means of the sustainable electrochemical CO_2 reduction (eCO_2R) towards formate (FA) is a promising strategy for CO_2 abatement, clearing the path towards a carbon neutral future. Currently, three possible reaction pathways have been identified for the eCO_2R towards FA, all of which are initiated by the adsorption of CO_2 on the electrocatalyst's surface. Therefore, a possible strategy to enhance the CO_2 availability near the active sites is to combine an active electrocatalyst material (here, SnO_2) with a known carbon capture medium (here, nitrogen-doped ordered mesoporous carbon (N-OMC)). SnO_2 was introduced *in situ* during the N-OMC synthesis, yielding SnO_2-N-OMCs. We approached the state-of-the-art for Sn-based N-doped carbon electrocatalysts in terms of performance under industrially relevant currents with an FE_{FA} of 59% for SnO_2-N-OMC (6) and 61% for SnO_2-N-OMC (2). Moreover, the SnO_2-N-OMC electrocatalysts require a low overpotential, courtesy of the N-OMC support, compared to the state-of-the-art, for the selective conversion of CO_2 towards FA at the industrially relevant current density of 100 mA cm^{-2}. Additionally, the 24 h stability of the best performing SnO_2-N-OMC electrocatalysts is explored and pulverization/agglomeration and *in situ* SnO_2 reduction are identified as major degradation pathways, allowing future research to be steered more accurately towards more stable Sn-based electrocatalysts

for the eCO_2R towards FA. An optimal combination of both the SnO_2 species and the N-OMC carbon capture medium could result in a synergistic effect, especially when utilization of the N-OMC support material is optimized to morphologically stabilize the SnO_2 active species.

Keywords

Nitrogen doped Ordered Mesoporous Carbon, SnO_2, Degradation Misms, Electrochemical CO_2 Reduction, Formate

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1. Introduction

Since the start of the second industrial revolution in the late 19th century, a rapid increase in anthropogenic CO_2 emissions has been supercharging Earth's natural greenhouse effect, making CO_2 Earth's most harmful and prevalent greenhouse gas, bringing about global warming, disrupted weather patterns and an acidification of the oceans [1–3]. Nonetheless, innovative negative carbon technologies such as Carbon Capture and Storage (CCS) or Carbon Capture and Utilization (CCU) are gaining momentum as they provide a promising strategy for CO_2 abatement, leading to an imperative carbon neutral future [4–7]. More than two decades ago, Hori *et al.* laid the groundwork for closing the anthropogenic carbon cycle by means of electrochemical CO_2 reduction (eCO_2R) towards value-added chemicals [8]. Utilizing renewable electricity and water, CO_2 is electrocatalytically reduced into various value-added products, such as carbon monoxide (CO), formate (FA, $HCOO^-$), methanol (CH_3OH) and ethylene (C_2H_4) [9]. Among these reaction products, formate, a 2-electron transfer liquid product, and CO, a gaseous product, currently have the potential to generate the highest revenue per mole of consumed electrons [10,11]. Furthermore, FA could play an important role as a means for future energy storage due to its use as a hydrogen or CO carrier [12]. Since Hori's pioneering work, numerous excellent metal-based electrocatalysts, such as Pb, Hg, Cd, Tl, Co, Sb, Bi, In and Sn have been found to be selective for the eCO_2R towards formate [8,13,14]. While Pb, Hg, Cd and Tl are harmful to the environment and have a high toxicity, Co and Sb-based electrocatalysts have only recently gained attention and are still in the early stages of research [13]. Unlike the aforementioned electrode materials, Bi-, In- and Sn-based electrocatalysts all have a low toxicity, are more environmentally friendly and currently yield the best electrochemical performances for the eCO_2R towards FA [15]. Due to their high selectivity (FE_{FA}), low toxicity, non-noble nature, ecological and inexpensive properties, Sn-based electrocatalysts are one of the most interesting candidates for the eCO_2R towards FA [16–18].

Currently, three possible reaction pathways have been identified for the eCO_2R towards FA, all of which are initiated by the adsorption of CO_2 on the electrocatalyst's surface [18,19]. Deng *et al*. recently uncovered that the rate-determining step (RDS) of these reaction pathways is this first step, the adsorption of CO_2 onto the electrocatalytic active site [20]. Consequently, in order to enhance the overall eCO_2R, the interaction, i.e. adsorption, between the slightly acidic CO_2 molecules and electrocatalyst surface has to be improved in order to fend off the competing hydrogen evolution reaction (HER) and to yield a high selectivity and productivity. This is frequently achieved in literature by incorporating nitrogen functional groups into carbon support materials [21]. Nitrogen-doped (N-doped) porous carbon materials are frequently used for efficient CO_2 capture, as the introduction of nitrogen into the carbon matrix increases the surface polarity and basicity, which results in enhanced CO_2 adsorption [21–23]. Introducing SnO_2, as a selective electrocatalyst towards FA, during the synthesis of N-doped carbons could also prove to simultaneously functionalize the carbon capture medium and facilitate the rate-determining CO_2 adsorption for the eCO_2R towards FA [24].

In the state of the art, a few other SnO_x N-doped carbon electrocatalysts with selectivities reaching up to 80% towards formate have been reported [24–26]. Zhang *et al.,* for example, decorated nitrogen-doped multiwalled carbon nanotubes (N-MWCNTs) with SnO_2 nanoparticles (SnO_2/N-MWCNTs), achieving an FE_{FA} of up to 46% at an applied potential of -0.9 V vs. Ag/AgCl, compared to only 10% for the supporting N-MWCNTs material, indicating that the incorporation of SnO_2 nanoparticles shifts the eCO_2R selectivity towards formate [27]. These observations were verified by Birdja *et al*., who revealed the ability of the metal center of metalloprotoporphyrins to tune the selectivity towards FA. In their research, they found that the Faradaic efficiency for formic acid increased with different metal centers, such as In and Sn [28]. Furthermore, Zhao *et al*., modified an N-doped carbon nanofiber with Sn species to obtain a tunable electrocatalytic performance towards either CO or formate, depending on the structure of the incorporated Sn species. In their research, they revealed that atomically dispersed Sn species drive the CO_2 conversion towards CO, while Sn nanoparticles promote the electrocatalytic conversion of CO_2 towards formate with a selectivity of 62% [29]. Moreover, Duarte *et al*. reported a tunable selectivity towards the desired eCO_2R product by altering the embedded transition metal in their metal-nitrogen-doped carbon electrocatalyst. With a partial current density of 70 mA cm^{-2}, their Sn-N-C catalyst achieved a Faradaic efficiency of 70% towards formate [30]. Finally, Fu *et al*., described an electrochemically exfoliated graphene supported 2D confined core-shell structured SnO_2 nanoparticle electrocatalyst, encapsulated into N-doped carbon. The combination of N dopants and a strong particle confinement effect resulted in a high FE_{FA} of 81.2% at -1.2 V [24].

Here, N-doped ordered mesoporous carbons (N-OMCs) are functionalized for the eCO_2R towards FA by introducing SnO_2 during the synthesis, yielding SnO_2-N-OMCs. Contrary to previous research, we

wanted to explore the interplay between SnO_2, which is well-known to be selective for the eCO_2R towards FA, and an N-OMC carbon capture medium as support material, which facilitates the rate-determining CO_2 adsorption. We investigated the influence of the introduction of an SnO_2 precursor during the N-OMC synthesis, while simultaneously revealing the influence of the N-OMC carbon capture medium and SnO_2 species on the electrochemical performance and studying their electrocatalytic stability and degradation pathways. We unravelled whether or not combining SnO_2 with an N-OMC carbon capture medium has a synergistic effect because of the enhanced CO_2 adsorption. To realize this, seven different (SnO_2-)N-OMC electrocatalysts were prepared with varying SnO_2 contents, incorporated during various synthesis steps, and with a variable specific surface area (S_{BET}). This allowed us to simultaneously investigate the influence of introducing the SnO_2 species on the morphology of the N-OMC, and more importantly, the influence of the N-OMC support material and SnO_2 species on the electrochemical performance for the eCO_2R towards FA. With a FE_{FA} of 59% for SnO_2-N-OMC (6) and 61% for SnO_2-N-OMC (2), we approached the state-of-the-art for Sn-based N-doped carbon electrocatalysts in terms of performance under industrially relevant currents. Furthermore, the SnO_2-N-OMC electrocatalysts require a lower overpotential, due to the N-OMC support, for the selective (± 60%) conversion of CO_2 towards FA at the industrially relevant current density of 100 mA cm^{-2}. Additionally, the 24 h stability of these best performing SnO_2-N-OMC electrocatalysts is explored and their most predominant degradation mechanisms are identified, allowing future research to be steered towards more stable Sn-based electrocatalysts.

2. Experimental

2.1 Materials

The following chemicals were used as received, without any further purification: acetone (99.5+%, a.r., Chem-Lab), ammonium peroxydisulfate (98%, Alfa Aesar), aniline (99.8%, pure, Acros Organics), 2,3-dihydroxynaphthalene (≥98.0%, Sigma-Aldrich), D520 NAFION® solution (Ion Power), glycerol (a.r., Fisher Scientific), hydrochloric acid (37%, a.r., Chem-Lab), hydrochloric acid (37%, Honeywell chemicals), hydrofluoric acid (40%, VWR chemicals), hydrogen peroxide (35%, Merck), nitric acid (67-70%, Avantor - J.T.Baker), ICP Multi-element standard solution IV (Merck), pluronic® P-123 (PEG-PPG-PEG, average Mn ~5.800, Sigma-Aldrich), potassium hydrogen carbonate (99.5+%, v.p., Chem-Lab), potassium hydroxide (85+%, pellets a.r., Chem-Lab), propanol-2 (99.8+%, iso-propanol a.r., Chem-Lab), sodium hydroxide (99+%, pellets a.r., Chem-Lab), tetraethyl orthosilicate (98%, Acros Organics), tin(II) chloride.2aq (98+%, a.r., Chem-Lab), tin plasma standard solution (Sn 1000ppm, Specpure, Alfa Aesar).

2.2 Synthesis

2.2.1 Preparation of the SBA-15 hard template

In a typical SBA-15 synthesis, 1.8 g Pluronic® P-123 and 1.8 g glycerol were stirred overnight in 69 g of a 1 M hydrochloric acid (HCl) aqueous solution, at 35 °C, in a polypropylene (Nalgene®) bottle. Next, 3.87 g tetraethyl orthosilicate (TEOS) was added dropwise to the mixture under vigorous stirring. Subsequently, the mixture was kept at 35 °C for an additional 24 h under static conditions. Afterwards, a hydrothermal treatment was performed at 100 °C for 24 h. Finally, the solid product was collected by filtration, washed with distilled water until a pH 4-5 was obtained, and dried overnight at 80 °C. The resulting white powder was calcined at 550 °C for 6h (1°C min^{-1}) in flowing air, in order to remove the organic structure directing agent (SDA) [31,32].

2.2.2 Fabrication of the SnO$_2$ nitrogen-doped ordered mesoporous carbon electrocatalyst

SnO$_2$ N-doped ordered mesoporous carbon (SnO$_2$-N-OMC) materials were prepared using a two-step procedure (Figure 1), inspired by and adapted from Wang et al. [33] and Sheng et al. [31], respectively. The SnO$_2$ precursor (SnCl$_2$.2H$_2$O) was included either completely during addition of the aniline or 2,3-dihydroxynaphthalene or divided between both steps, as depicted in figure 1. A detailed overview of the performed syntheses can be found in Table 1.

As a first step, aniline was polymerized inside the pores of the SBA-15 hard template. The amount of aniline incorporated in this step was selected in order to cover the SBA-15 surface with an aniline monolayer [31]. Approximately 0.5 g of the SBA-15 hard template was added to ±200 mL of the 0.5 M HCl aqueous solution and stirred for 15 minutes. Afterwards, the appropriate amount of aniline, calculated from the mass and specific surface area (S$_{BET}$) of the SBA-15 hard template and cross-sectional area (43 Å^2) and density (1.02 g cm^{-3}) of aniline, was added and the whole mixture was stirred for 1 h in an ice bath. Finally, a 1.2 molar excess of the radical initiator, ammonium peroxydisulfate (APS), dissolved in ±50 mL of the 0.5 M HCl aqueous solution, was added and the mixture was stirred for 24 h in an ice bath. Afterwards, the solvent was removed in a rotary evaporator and the sample was dried in an oven at 100 °C. The sample was then placed into the tubular furnace where it underwent a pyrolysis for 3 h at 900 °C (3.3 °C min^{-1}) under constant Argon (Ar) flow (1 cm³ s^{-1}). In the second step of the synthesis, the remaining pore volume of the SBA-15 was loaded with carbon. The required amount of 2,3-dihydroxynaphthalene (2,3-DHN) was calculated using the remaining pore volume of the SBA-15 hard template and the density of 2,3-DHN (1.33 g cm^{-3}). The, as obtained grey solid, from the first step was mixed with the appropriate amount of 2,3-DHN in acetone, and was allowed to stir at room temperature for 24 h. After evaporation of the solvent, the composite material was thermally treated for 2 h at 300 °C (3.3 °C min^{-1}) under a continuous Ar flow (1 cm³ s^{-1}), before washing the sample with acetone 3 times, collecting it by filtration and drying it overnight. A final

pyrolysis was then performed at 900 °C (3.3 °C min^{-1}) for 5 h under an Ar atmosphere (1 cm³/s). Finally, the silica template was removed by suspending the as obtained black solid in a 2M sodium hydroxide aqueous solution while stirring for 8 h at 100 °C under reflux. The SnO$_2$-N-OMC material was collected in the form of a black solid by filtration and was dried at 100 °C [31,32].
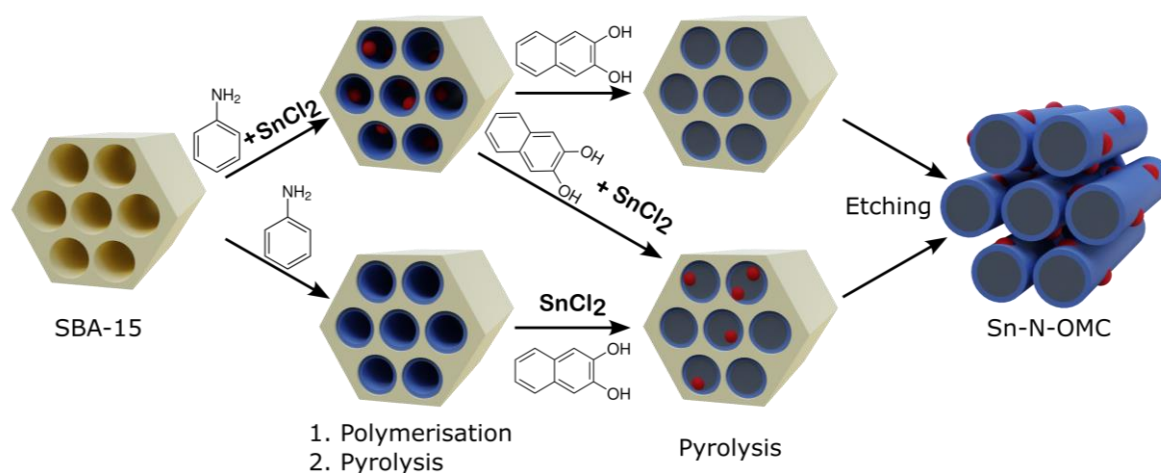

Figure 1. Synthesis method SnO$_2$ nitrogen-doped ordered mesoporous carbon electrocatalysts

Table 1. Detailed overview (SnO$_2$-)N-OMC Syntheses

Catalyst	Hard Template	Aniline (mL)	APS (g)	2,3-DHN (g)	SnCl$_2$.2H$_2$O (g)	Step
N-OMC (1)	SBA-15 (1)	0.182	0.5454	0.7000	0	/
SnO$_2$-N-OMC (1)	SBA-15 (2)	0.185	0.5557	0.6982	0	Aniline
					0.1	2,3-DHN
SnO$_2$-N-OMC (2)	SBA-15 (3)	0.179	0.5364	0.6491	0.4	Aniline
					0	2,3-DHN
SnO$_2$-N-OMC (3)	SBA-15 (4)	0.182	0.5454	0.6366	0.3	Aniline
					0.1	2,3-DHN
SnO$_2$-N-OMC (4)	SBA-15 (5)	0.221	0.6618	0.7788	0	Aniline
					0.4	2,3-DHN
SnO$_2$-N-OMC (5)	SBA-15 (6)	0.179	0.5374	0.6778	0.1	Aniline
					0.3	2,3-DHN
SnO$_2$-N-OMC (6)	SBA-15 (7)	0.168	0.5035	0.6323	0.2	Aniline
					0.2	2,3-DHN

2.3 Physicochemical Characterization

Nitrogen physisorption was performed at 77 K, utilizing a Quantachrome Quadrasorb SI (Quantachrome Instruments, Boynton Beach, FL, USA) automated surface area & pore size analyzer.

Prior to all N_2 physisorption measurements, all samples were degassed at 200 °C for 16 h. The specific surface area (S_{BET}) was calculated using the Brunauer-Emmet-Teller (BET) equation and Quantachrome QuadraWin software. **X-ray Powder Diffraction (XRD)** was evaluated using a Bruker D8 ECO powder diffractometer with a LYNXEYE XE-T detector and Cu K-Alpha radiation. SBA-15 samples were probed from 0.5 – 20° 2θ, while all (Sn) N-OMC samples were measured from 20 – 80° 2θ and compared with the crystallography open database (COD) #1534785 for tetragonal SnO_2. **Raman spectroscopy** was performed using a Micro-Raman Horiba (Xplora Plus Microscope) equipped with a 532 nm green laser. Raman spectra were recorded from 750 – 2000 cm^{-1} Raman shift in order to investigate the degree of graphitization. All samples were measured, coated on a glass slide to avoid interference of the carbon based gas diffusion electrode. **X-ray Photoelectron Spectroscopy (XPS)** was performed on a PHI-VersaProbe III, equipped with an Al Kα (1486.6 eV) monochromatic X-ray source. An area of Ø 100 μm was measured, using a pass energy of 26 eV for the high-resolution (HR) spectra and an automatic neutralizer. The wt% is calculated from the atomic concentrations, based on internal standards in the PHI MultiPak software. The high resolution C1s, O1s, N1s and Sn3d5 XPS spectra were processed using the PHI MultiPak software. **Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES)** was performed on a PerkinElmer Optima 8300 after digestion of the samples in a Milestone Ethos UP microwave digestion system. All (SnO_2-)N-OMC samples were analyzed in two-fold. To this extent, 10 mg of each sample was weighed out in a Teflon microwave vessel after which 2 mL of H_2O_2, 8 mL of HNO_3 and 3 mL of HF were added to each vessel. The vessels were left overnight and underwent microwave digestion the following day. After the first digestion, an additional 1 mL of H_2O_2 and 2 mL of HF were added and the microwave digestion was repeated a second time. Finally, 2 mL of HNO_3 and 1 mL of H_2O_2 were added for a third microwave digestion and the digested content of the vessels was transferred and diluted to 50 mL. Before the ICP-OES analysis, the samples were diluted 10 times with 5% HNO_3. A blank sample of acids and a calibration series ranging from 5 ppb to 10 ppm of tin and multi-element standards were used for analysis. **High Angle Annular Dark-Field Scanning Transmission Electron Microscopy** (HAADF-STEM) as well as **Energy Dispersive X-ray Spectroscopy** (EDS) was performed using an aberration-corrected cubed ThermoFisher Scientific Titan transmission electron microscope operating at 200 kV, equipped with the ChemiSTEM system [34]. HAADF-STEM was performed *ex situ* after the electrochemical measurements, by scraping the samples off of the GDE, suspending them in ethanol and dropcasting them on Ultra Thin Film (UTF) carbon-coated Cu TEM grids. The **CO_2 adsorption capacity** was determined by means of **TGA**, using a NETZSCH STA 449 F3 Jupiter with a rhodium furnace. Prior to the measurements, all samples were pretreated under an inert nitrogen atmoshepere to desorb all adsorbed species. Afterwards, CO_2 was allowed to adsorb onto the samples by keeping them isothermal at 30°C for 4 hours under a 100 sccm N_2 and 33 sccm

CO_2 flow. Finaly, the samples were reheated to 200°C at a rate of 10 °C min^{-1} under 100 sccm N_2, remaining isothermal at 200°C for 2 hours under 100 sccm N_2 to allow all CO_2 to be desorbed before being cooled down to 30°C under an inert N_2 atmosphere.

2.4 Electrochemical Measurements

2.4.1 Uncompensated Resistance Determination

The **uncompensated resistance R_u (Ohmic drop)**, was determined by means of a current interrupt measurement, prior to the electrochemical CO_2 reduction experiments. A potential of -4 V vs. Ag/AgCl was applied before triggering the current interrupt circuit and measuring the potential decay over a time period of 2 ms. The uncompensated resistance was obtained from a linear regression between 0 s and 500 µs in the Metrohm Autolab Nova 2.1.5 Software, and was consistently between 7 to 10 Ω for all measurements. The utilized Ag/AgCl refererence electrode is regularly checked versus our ground Ag/AgCl reference electrode. All reported potentials were corrected for this resistance after measurement and converted to the RHE scale.

2.4.2 Electrochemical CO_2 Reduction

Gas diffusion electrodes (GDEs) are prepared by spray coating a 25 cm² Sigracet 39 BB GDE with an ink made from the synthesized electrocatalyst powders. For deposition with a target electrocatalyst loading of 1.5 ± 0.1 mg cm^{-2}, the ink consists of 75 mg of the as-synthesized (SnO_2-)N-OMC electrocatalyst, and 0.375 g of a 5 wt% Nafion solution in approximately 10 mL of a 1:1 Milli-Q (18.2 MΩ·cm @ 25 °C):IPA solution. Afterwards, the GDE is divided into 6 smaller GDEs, which are used as cathodes in a small flow-by electrolyzer with a geometric electrochemically active surface area of 1 cm². The flow-by electrolyzer consists out of two backplates, PMMA insulators, copper current collectors, a graphite cathodic compartment and an adjacent PMMA catholyte flow field with reference electrode, a graphite anodic compartment and several gaskets for appropriate sealing of the electrolyzer. A full schematic representation of the utilized flow-by electrolyzer and setup is provided in the supporting information (Figure S1).

Electrocatalytic CO_2 reduction experiments of both 1 and 24 hours were conducted by applying a current density of -100 mA cm^{-2} to the aforementioned flow-by electrolyzer. The 0.5 M $KHCO_3$ catholyte is fed single pass at a flow rate of 2 mL min^{-1}, while the 2 M KOH anolyte is recycled at an equal flow rate. Pure CO_2 is fed through the backside of the GDE at a flow rate of 15 mL min^{-1}, which was determined to be the ideal flow rate to achieve the highest FE% for the eCO$_2$R. A Ni foam is used as counter electrode (anode), and a Nafion 117 membrane and Ag/AgCl reference electrode were used. Liquid samples were taken, for a period of 2 minutes, after 15 minutes and after 1 hour to

determine the FE% towards formate by means of HPLC. Gaseous products were detected by means of in-line GC. For the long-term 24 h electrolysis experiments, additional samples were taken during the first 6 hours of the reaction and once again after 24 h. The reported data was reproduced and an average value is reported for all FE_{FA} and iR-compensated potentials.

3. Results and Discussion

3.1 Physicochemical Characterization

Similar to the SBA-15 hard template (physicochemical characterization in SI, Figure S2 and S5A, B), N-OMC materials are known to have a well ordered, high specific surface area [31,32]. The effect of incorporating SnO_2 species during the synthesis on the specific surface area and structure of the N-OMC support material was investigated by nitrogen physisorption, utilizing the BET equation. The adsorption-desorption isotherms of all (SnO_2-)N-OMCs, as depicted in Figure 2, are classified as a composite Type IVa + Type II isotherm with a clear hysteresis.
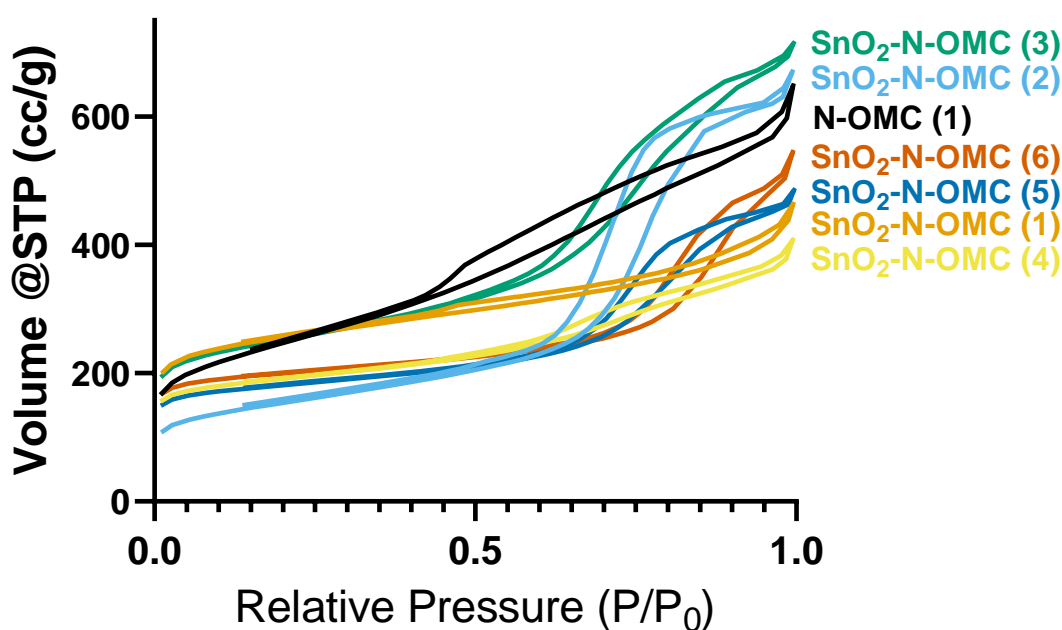
Figure 2. Nitrogen adsorption-desorption isotherms (SnO_2-)N-OMC electrocatalysts

Type IVa isotherms are indicative of mesoporous adsorbents and typically end in a final, nearly horizontal, saturation plateau near $P/P_0 = 1$. Type II isotherms, on the other hand, are characterized by the unrestricted monolayer-multilayer adsorption on nonporous or macroporous adsorbents, resulting in the absence of a plateau near $P/P_0 = 1$. Given that the adsorbed amount appears to increase infinitely when $P/P_0 = 1$, indicating either interparticle adsorption or the presence of macropores, but

hysteresis does manifest, pointing towards mesopores, all samples were classified as a composite Type IVa + Type II isotherm. According to the recommendation in the IUPAC technical report, the total pore volume of such a composite Type IVa + Type II isotherm cannot accurately be evaluated since the isotherm is not horizontal near $P/P_0 = 1$. Nevertheless, the pore volume was derived from the adsorbed amount close to unity (i.e. $P/P_0 \approx 0.95$) by means of the Barrett, Joyner and Halenda (BJH) method for an indication [35]. The specific surface areas and corresponding pore volumes and sizes are summarized in Table 2. The BET surface area and pore size distribution plots are provided in the supporting information (Fig. S3).

Based on the adsorption-desorption isotherms, SnO_2-N-OMC (1) and SnO_2-N-OMC (4) appear to be the only two samples with a less neatly ordered mesoporous structure, though they still have high specific surface areas, as their isotherms have a higher resemblance to a Type II isotherm for nonporous or macroporous materials. Nonetheless, both SnO_2-N-OMC (1) and SnO_2-N-OMC (4) isotherms contain hysteresis, indicating the presence of cylindrical (meso)pores, larger than ~4 nm [35]. Interestingly, these are the only two SnO_2-N-OMC samples where the entirety of the $SnCl_2$ precursor was added simultaneously with the 2,3-dihydroxynaphthalene. All other SnO_2-N-OMC adsorption-desorption isotherms have a closer resemblance to a Type IVa isotherm, indicating well-ordered mesoporous materials. These observations seem to imply that it's important to at least add a part of the $SnCl_2$ precursor with the aniline and that adding the entire $SnCl_2$ precursor during the 2,3-DHN step appears to hinder the formation of a neatly ordered mesoporous carbon structure. Low angle XRD of the resulting (SnO_2)-N-OMC electrocatalysts (Fig. S4), however, only weakly indicates a neatly ordered mesoporous structure for some of the supporting N-OMC materials. Nevertheless, with the nitrogen adsorption-desorption isotherms and visual confirmation, obtained via electron microscopy (Fig. S5), we can confirm that all SnO_2-N-OMC electrocatalysts possess areas which are neatly ordered and others that are amorphous due to the incorporation of the $SnCl_2$ precursor during the synthesis.

For Type II and Type IVa isotherms, the linearity of the BET plot is limited to a part of the isotherm, most commonly in the relative pressure range of $\sim 0.05 - 0.30$. However, for our SnO_2-N-OMC materials, this BET range is shifted towards lower relative pressures due to the high adsorption energy of the nitrogen on the graphitized carbon [35].

Table 2. Morphological properties of the (SnO$_2$-)N-OMC electrocatalysts

Catalyst	S$_{BET}$ (m² g^{-1})	Pore volume (cm³ g^{-1})*	Pore size (nm)**
N-OMC (1)	856	0.88	-
SnO$_2$-N-OMC (1)	952	0.63	-
SnO$_2$-N-OMC (2)	547	0.96	7.0
SnO$_2$-N-OMC (3)	925	1.05	4.5
SnO$_2$-N-OMC (4)	722	0.56	-
SnO$_2$-N-OMC (5)	689	0.70	4.1
SnO$_2$-N-OMC (6)	767	0.74	3.9

* The pore volume was derived from the adsorbed amount close to unity (i.e. P/P$_0$ ≈ 0.95) by means of the Barrett, Joyner and Halenda (BJH) method to get an indication since it is conventionally not determined for composite Type IVa + Type II isotherms.

**Not all pore sizes could be determined using the BJH method because of the composite Type IVa + Type II isotherms.

The as-synthesized SnO$_2$-N-OMC materials have a varying surface area, pore volume and pore size. Here, it is again apparent that both the SnO$_2$-N-OMC (1) and SnO$_2$-N-OMC (4) electrocatalysts have a less neatly ordered mesoporous structure with the lowest pore volumes. Nevertheless, according to these physisorption results, all SnO$_2$-N-OMC electrocatalysts possess a high surface area (> 500 m² g^{-1}) and a high volume of (meso)pores, which is promising for their role as CO$_2$ capturing agents. This variety in S$_{BET}$, which is (partially) inherent to the SnO$_2$-N-OMC synthesis, allows us to explore the influence of the N-OMC support material on the electrochemical performance of the SnO$_2$ species for the eCO$_2$R towards formate.

Information related to the degree of graphitization (i.e. the ratio of the areas of the D and G bands) and knowledge concerning the crystalline structure, chemical nature and space group symmetry were obtained by Raman spectroscopy and XRD, respectively. The normalized Raman spectra (Figure 3) display two broad peaks at 1350 cm^{-1} and 1600 cm^{-1}, the former usually referred to as the D-band, originating from edge defects of the graphitic domain, and the latter identified as the G-band, which is assigned to planar vibration of sp^2 carbon atoms in an ideal graphitic layer [31,36,37]. Since the ratio of the areas of the D and G bands (I$_D$/I$_G$), which is inversely proportional to the degree of graphitization, is > 1 and comparable for all samples, we can conclude that all SnO$_2$-N-OMC electrocatalysts have a clear graphitic character, despite amorphous segments. The addition of an SnO$_2$ precursor during the N-OMC synthesis had no major influence on the resulting degree of graphitization of the N-OMC [31].
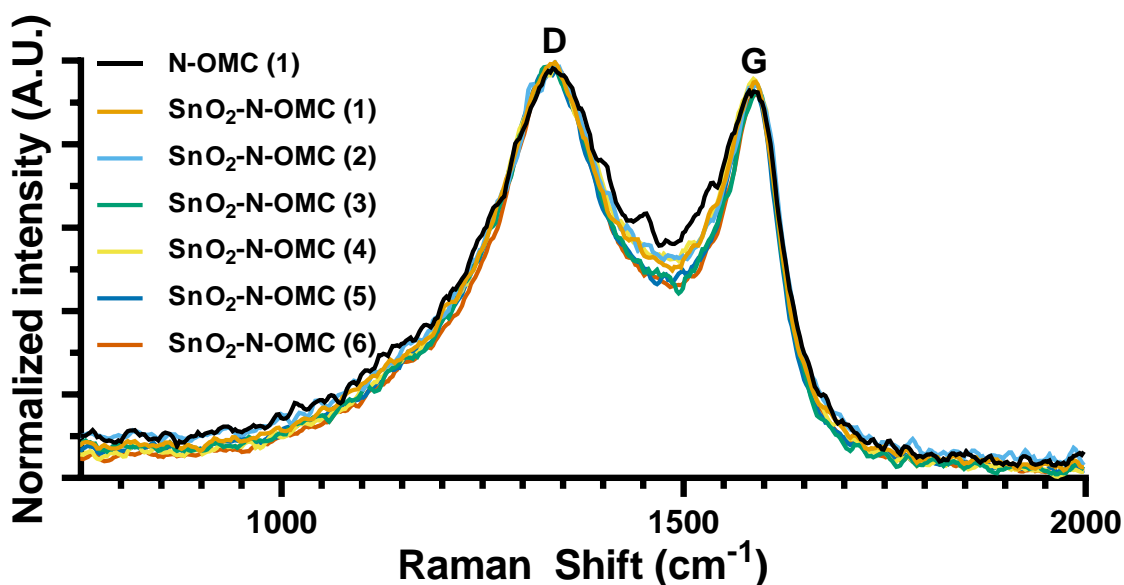
Figure 3. Normalized Raman spectra of the as-synthesized (SnO$_2$-)N-OMC electrocatalysts, recorded between 750 and 2000 cm^{-1} with a 532 nm green laser

The wide angle diffractograms (Figure 4) display the typical diffraction pattern with peaks at $2\theta = 26.5°$, 33.8°, 37.9°, 38.9°, 42.6°, 51.7°, 54.7°, 57.7°, 61.8°, 64.6°, 65.8°, 71.1° and 78.5°, present in all SnO$_2$-N-OMC samples. These peaks are attributed to reflections of the (110), (101), (200), (111), (120), (211), (220), (002), (130), (112), (301), (202) and (321) planes, respectively, of tetragonal SnO$_2$ (COD #1534785) [38,39]. Additionally, two broad and weak peaks are observed in the N-OMC diffractogram at approximately 25° and 43.5° 2θ, which correlate to amorphous carbon and are also observed in the diffractograms of the SnO$_2$-N-OMC catalysts [40]. Again, no distinctive differences are observed in terms of the crystalline structure and chemical nature of the SnO$_2$ species, which are all confirmed to be tetragonal SnO$_2$. This allows for differences in the electrochemical performance to be attributed solely to the morphology of the SnO$_2$ species, SnO$_2$ loading and influences of the N-OMC support material.
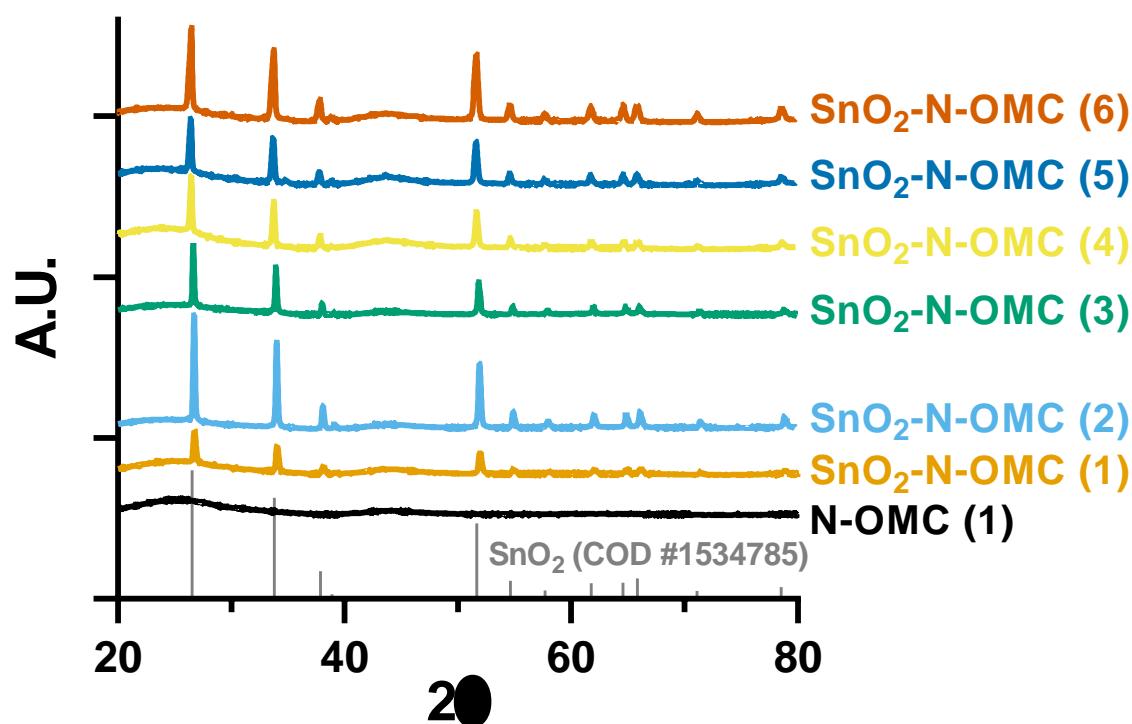
Figure 4. Wide angle X-ray diffractogram of the as-synthesized (SnO$_2$-)N-OMC catalysts, compared with the Crystallography Open Database (COD) #1534785 for tetragonal SnO$_2$.

3.2 Electrochemical CO$_2$ Reduction

The electrochemical performance of the (SnO$_2$-)N-OMC electrocatalysts was investigated in a small flow-by electrolyzer with a geometric surface area of 1 cm² (Figure S1). By performing a 1 h chronopotentiometric experiment at a constant applied current density of 100 mA cm^{-2}, the average iR-compensated cathodic operating potential (Figure 5a) and FE$_{FA}$ (Figure 5b) were determined. The overall average FE% for all seven electrocatalysts has been provided in the SI (Fig. S6), showing no other detectable products being formed other than formate, hydrogen and carbon monoxide. Furthermore, it approaches a total FE (%) of approximately 100% when taking into account the inherent error margins of all separately reported Faradaic Efficiencies.
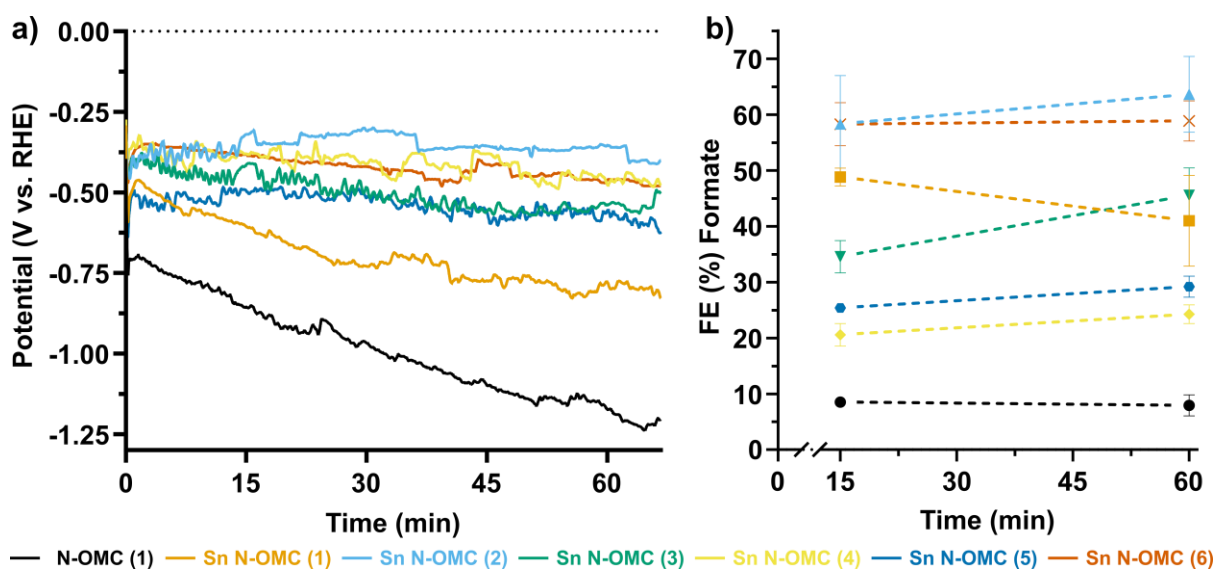
Figure 5. a) average iR-compensated potential (V vs. RHE) and b) average FE% towards formate with error bars, plotted as a function of time at a constant current density of 100 mA cm^{-2} for 1 h.

Several trends are observed when looking at the electrocatalytic performance and Faradaic Efficiency towards FA of the (SnO_2-)N-OMCs. First, the pristine nitrogen doped ordered mesoporous carbon material (N-OMC (1)) has a low average FE_{FA} of 8% and a continuously increasing cathodic potential over the course of 1 h, indicating that, on its own, it is not suited for the electrochemical reduction of CO_2 to formate. Interestingly, this trend of an increasing cathodic potential appears to diminish by combining the N-OMC with SnO_2 species, as evidenced by the potential-time curves of the SnO_2-N-OMC electrocatalysts. SnO_2-N-OMC (1) has the lowest amount of SnO_2 and already exhibits a significantly smaller slope. Moreover, upon further increasing the SnO_2 content, a constant cathodic potential is achieved. Therefore, this continuously increasing cathodic potential is hypothesized to originate from the blocking of active sites due to inefficient conversion of adsorbed CO_2 by the N-OMC or the competing HER which increases the local pH, resulting in fewer protons and an increasing potential to maintain a constant current at low FE_{FA}.

Additional measurements of the most stable and best performing SnO_2-N-OMC (2) electrocatalyst, with varying CO_2 and N_2 mixed flows (Figure S7), revealed a stable uncompensated potential for both the eCO_2R (100/0, $CO_2/N2$) and HER (0/100, CO_2/N_2). When forcing a combination of the eCO_2R and HER (50/50, CO_2/N_2), however, the FE_{FA} drops to approximately 35% and a similar continuously increasing cathodic potential is observed.

Furthermore, the CO_2 adsorption capacity of the pristine N-OMC (1), best performing SnO_2-N-OMC (2) and worst performing SnO_2-N-OMC (4) electrocatalysts were determined by means of TGA and compared to the equally porous, non-nitrogen doped, commercially available Ensaco® carbon black (S_{BET} 770 m² g^{-1}). With 0.291 mmol g^{-1}, the Ensaco® carbon black adsorbed the lowest amount of CO_2,

while the pristine N-OMC (1) is able to adsorb approximately 2.5 times the amount of CO_2 (0.725 mmol g^{-1}). Both SnO_2-N-OMC electrocatalysts adsorbed 0.710 mmol g^{-1} and 0.834 mmol g^{-1} for SnO_2-N-OMC (2) and SnO_2-N-OMC (4), respectively. Normalized to their specific surface area (S_{BET}), Ensaco® carbon black and the pristine N-OMC (1) adsorbed 0.378 µmol m^{-2} and 0.847 µmol m^{-2}, respectively, verifying the previously hypothesised increased CO_2 adsorption by incorporating nitrogen into the supporting carbon material. Furthermore, the best performing SnO_2-N-OMC (2) adsorbed more CO_2 (1.299 µmol m^{-2}) than SnO_2-N-OMC (4) (1.155 µmol m^{-2}), revealing that by incorporating SnO_2 species, the CO_2 adsorption capacity is increased even further.

Combining these results indicates that, while both hypotheses contribute to the continuously increasing cathodic potential, for the SnO_2 containing N-OMC electrocatalysts, the latter hypothesis is the most predominant cause. The continuously increasing cathodic potential for N-OMC (1), under continuous CO_2 flow, however, is dominated by the blocking of active sites (for the HER) due to inefficient conversion of the adsorbed CO_2.

The addition of SnO_2 species boosts the electrocatalytic selectivity towards formate from 8% for the blank N-OMC (1) to 59% and 61% for the SnO_2-N-OMC (6) and SnO_2-N-OMC (2) electrocatalysts, respectively, approaching the state-of-the-art of comparable materials (Table S1). The combination of high current densities and low overpotentials with a selectivity of around 60% puts our materials at the same level or above the state-of-the-art in the field. The SnO_2 species are thus far more active for the eCO_2R towards FA and appear to predominantly determine the electrochemical performance, suppressing the electrochemical behavior of the N-OMC which was initially expressed by the continuously decreasing potential and a low selectivity towards formate. Finally, a latency effect is noticed in the FE_{FA} of most SnO_2-N-OMC electrocatalysts, presumably caused by the longer formate diffusion times, away from the active SnO_2 sites, through the mesoporous N-OMC supporting material [41].

Table 3. Composition of the (SnO₂-)N-OMC electrocatalysts in wt%, as determined by a) ICP-OES and b) XPS

Catalyst	Sn^a (wt%)	Sn^b (wt%)	C^b (wt%)	N^b (wt%)	O^b (wt%)
N-OMC (1)	0.08	0.00	90.27	2.06	7.67
SnO₂-N-OMC (1)	0.27	-	-	-	-
SnO₂-N-OMC (2)	1.15	2.47	90.91	0.32	6.30
SnO₂-N-OMC (3)	0.55	-	-	-	-
SnO₂-N-OMC (4)	0.69	3.33	87.79	0.98	7.90
SnO₂-N-OMC (5)	1.01	-	-	-	-
SnO₂-N-OMC (6)	0.57	4.44	86.00	0.22	9.34

In terms of selectivity, a wide variety, ranging from an average 22% for SnO₂-N-OMC (4) to 61% for SnO₂-N-OMC (2), was obtained by incorporating equal amounts of SnO₂ precursor during different steps of the N-OMC synthesis. ICP-OES and XPS analysis (Table 3 and Figure S8), however, revealed that while equal amounts of Sn precursor were added in most of the syntheses, most of the Sn wasn't retained in the final material, providing a widely varying amount of SnO₂ that was actually included. Moreover, upon comparing the Sn content, as determined by ICP-OES and XPS, it becomes clear that most of the Sn is present on the surface of the SnO₂-N-OMC electrocatalyst material and not incorporated inside the mesoporous carbon structure. Low and high magnification HAADF-STEM imaging combined with EDS elemental mapping confirmed the presence of a wide variety of SnO₂ species, ranging from large irregular SnO₂ species to differently sized SnO₂ nanoparticles, as depicted in figure S9, all of them having the rutile tetragonal SnO₂ structure (space group: P4₂/mnm). These SnO₂ species are mostly found at the outer part of the mesoporous carbon support. In addition, crystalline and non-crystalline atomic clusters, which have a significantly higher contrast compared to their background in high resolution HAADF-STEM images, lay among the N-OMC matrix. EDS elemental mapping of these clusters only showed carbon and silicon signals from the N-OMC, without a clear presence of Sn. This spectroscopy based result can be attributed to the small size of these clusters and their sensitivity under the electron beam, which only allowed us to use very short acquisition times. However, the analysis of the high resolution data of these crystalline clusters (Figure S9B) confirms that, similar to the bigger SnO₂ species (Figure S9C, F),[29] the interatomic distances are in agreement with the d-spacings of rutile SnO₂, a strong indication that they are Sn-based.

SnO₂-N-OMC (2) and SnO₂-N-OMC (6), respectively, enclose considerably larger irregular SnO₂ species and differently sized SnO₂ nanoparticles, than the least performing electrocatalyst, SnO₂-N-OMC (4). Considering that Zhao *et al*. reported atomically dispersed Sn species to promote the eCO₂R towards

CO and Sn nanoparticles are more selective towards formate, it is obvious that the large irregular SnO_2 species and/or the SnO_2 nanoparticles of different sizes are crucial and dominate the electrochemical performance of the SnO_2-N-OMC electrocatalysts when formate is the target product [29]. The moderate electrochemical performance of the other three SnO_2-N-OMC electrocatalysts (1, 3 and 5) highlights that the morphology of the SnO_2 species appears to be more important than the SnO_2 loading. Nonetheless, these SnO_2-N-OMC electrocatalysts seemingly have less selective SnO_2 species, compared to the best performing SnO_2-N-OMCs, resulting in a lower selectivity towards FA.

In summary, the observed electrochemical performance of the SnO_2-N-OMC electrocatalysts is a result of the combined behavior of the N-OMC (S_{BET} surface area, N-dopant, conductivity, etc.) support and the different SnO_2 species. As demonstrated, the N-OMC material independently isn't suited for the selective eCO_2R towards FA, which is why the SnO_2 species make the largest contribution to the electrochemical performance (especially selectivity) of the SnO_2-N-OMC electrocatalysts. Furthermore, the enhanced CO_2 adsorption, due to the N-OMC support material appears to positively influence the overpotential, in comparison to the state-of-the-art (Table S1). As a result, all SnO_2-N-OMC electrocatalysts demand a lower overpotential for the conversion of CO_2 towards FA at the industrially relevant current density of 100 mA cm^{-2}. The N-OMC support material itself, requires the largest overpotential, as depicted in Figure 5a, presumably caused by the poor conversion of the more easily adsorbed CO_2. However, we've demonstrated that we are able to significantly increase the FE_{FA} and lower the overpotential, utilizing a minimal amount of SnO_2 species, with the most selective morphologies being large irregular SnO_2 species and heterogeneous SnO_2 nanoparticles. An optimal combination of both SnO_2 species and the N-OMC carbon capture medium could thus result in a synergistic effect for the eCO_2R towards FA.

The long-term electrocatalytic performance and degradation pathways of the two best performing electrocatalysts (SnO_2-N-OMC (2) and SnO_2-N-OMC (6)) were evaluated by performing a 24 h chronopotentiometric experiment at an applied current density of 100 mA cm^{-2}, combined with *ex situ* HAADF-STEM imaging. After starting at a similar FE_{FA} of approximately 60%, the SnO_2-N-OMC (2) and SnO_2-N-OMC (6) electrocatalysts started to display a difference in stability after only 2 h of electrolysis at 100 mA cm^{-2}, as depicted in Figure 6. The FE_{FA} of SnO_2-N-OMC (2) increases to an average of 64% over the course of the first 6 hours, while the selectivity of the SnO_2-N-OMC (6) decreases to 28% after 6 h and even further to 12% at –0.95 V vs. RHE after 24 h. Eventually, after 24 h of operation, the FE_{FA} of SnO_2-N-OMC (2) decreases to an average of 43% at an operating potential of -0.60 V vs. RHE. *Ex situ* HAADF-STEM imaging of both electrocatalysts after 24 h of electrolysis (Figure 7A, B) reveals the morphological degradation of the large SnO_2 species, which are pulverized and agglomerated, similar

to the deterioration reported by Wu *et al*. [42] and described in our previous publication concerning pomegranate-structured SnO$_2$(@C) electrocatalysts [43].
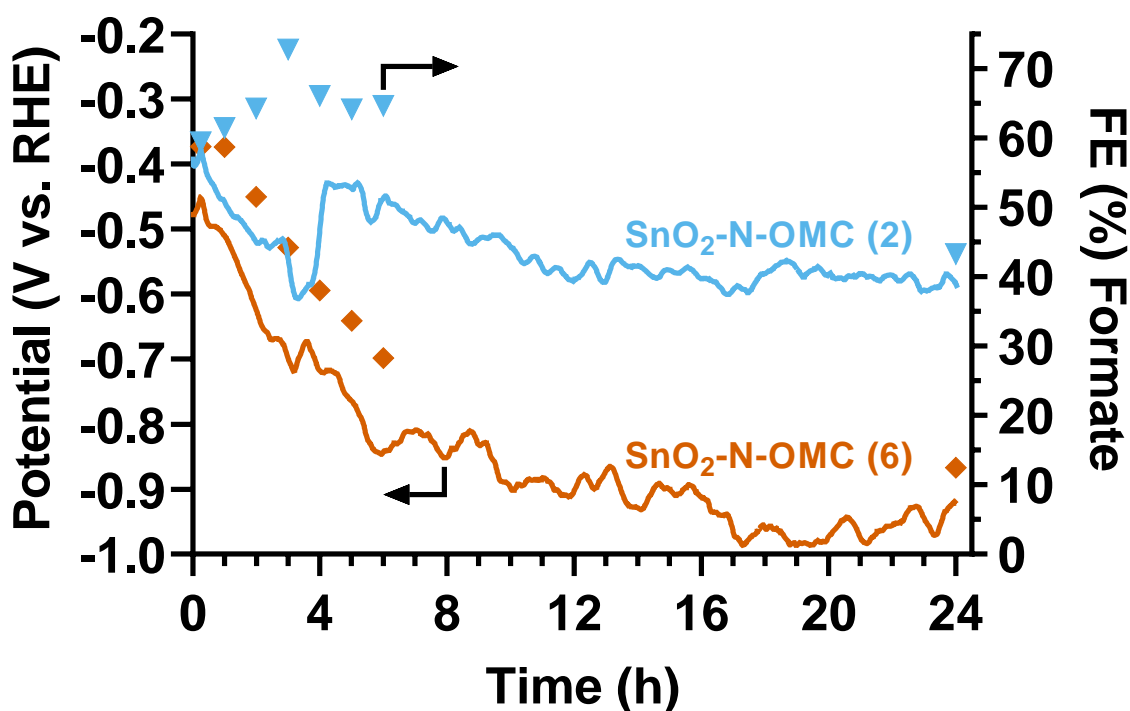

Figure 6. average iR-compensated potential (V vs. RHE) and FE% towards formate of the SnO$_2$-N-OMC (2) and SnO$_2$-N-OMC (6) electrocatalysts, plotted as a function of time at a constant current density of 100 mA cm^{-2} for 24 h.

This dissimilar electrocatalytic performance can be ascribed to a combination of morphological (pulverization and agglomeration) and chemical (*in situ* SnO$_2$ reduction towards metallic Sn) deterioration. Similar to the previously reported pomegranate-structure SnO$_2$ electrocatalyst, the loss of selectivity of the SnO$_2$-N-OMC (2) electrocatalysts due to the *in situ* SnO$_2$ reduction, is temporarily offset by the pulverization providing additional SnO$_2$ active sites for the eCO$_2$R towards FA. In the case of SnO$_2$-N-OMC (6), the initial SnO$_2$ species were already significantly smaller than the ones present in SnO$_2$-N-OMC (2), leading towards less pulverization (and more agglomeration) and consequently to less fresh SnO$_2$ sites being formed to offset the *in situ* SnO$_2$ reduction and more rapid loss in selectivity as a result (Figure 6).

This was further confirmed by postmortem *ex situ* XRD (Figure S10), which shows a decrease in the intensity of the diffraction pattern for tetragonal SnO$_2$ (COD #1534785) at the expense of an increase in the intensity of metallic Sn (COD #9008570) [44]. Furthermore, the appearance of additional peaks is observed, which can be attributed to KHCO$_3$ (COD #9016304) as a result of salt deposition during the eCO$_2$R [45]. This *in situ* SnO$_2$ reduction to metallic Sn (space group: I4$_1$/amd), observed by *ex situ* XRD and HAADF-STEM imaging and the corresponding Fourier Transform pattern, combined with

quantified (for atomic %) EDS elemental mapping (Figure 7C, D) in both SnO_2-N-OMC electrocatalysts after 24 h of electrolysis, is determined to be the most detrimental degradation pathway, resulting in the direct loss of selectivity. While morphological stability of the Sn-based electrocatalyst is important in the long run, chemical stability to withstand *in situ* SnO_2 reduction appears to be more crucial as this directly correlates to a severe loss in selectivity.
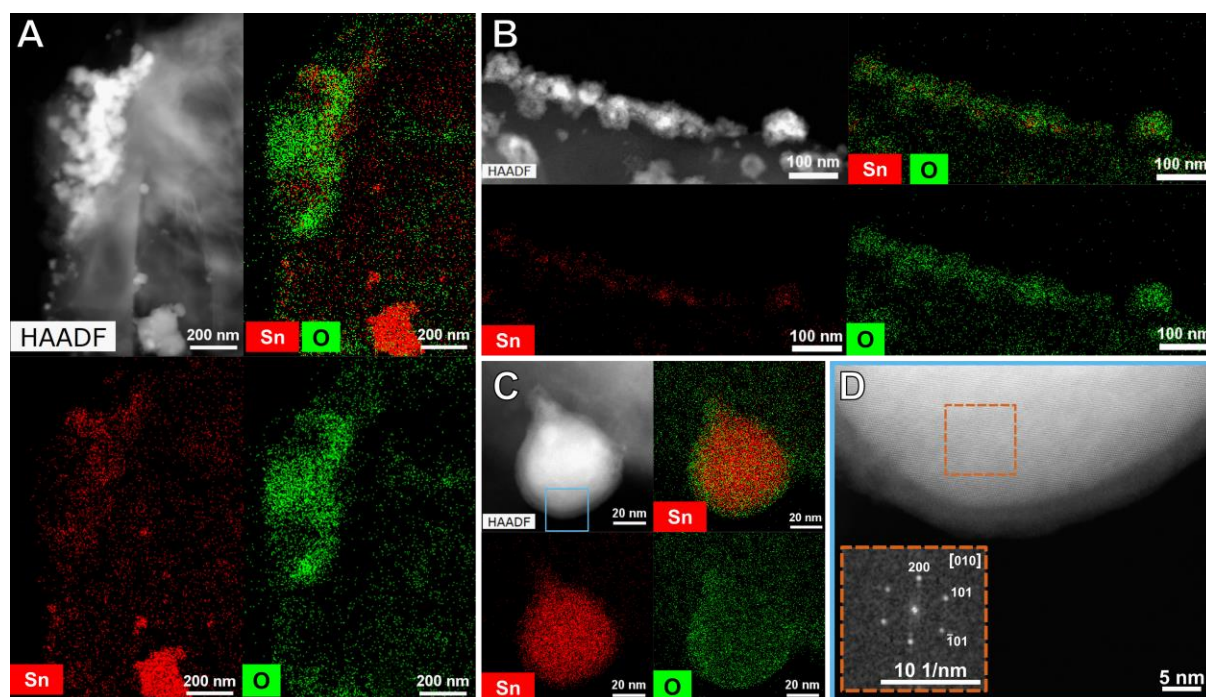

Figure 7. HAADF-STEM images and EDS elemental maps quantified for atomic % of A) SnO_2-N-OMC (2), B) SnO_2-N-OMC (6) after 24 h of electrolysis at 100mA cm^{-2} and C, D) HAADF-STEM images with the corresponding FT pattern and EDS elemental maps quantified for atomic % of a partially re-oxidized in situ reduced Sn nanoparticle in SnO_2-N-OMC (2).

To date, no universal consensus concerning the active site of SnO_2-based electrocatalysts and the reaction mechanism for the eCO_2R towards formic acid has been reached in state-of-the-art literature. Nonetheless, it is obvious that oxides play an important role in their electrocatalytic performance. In literature, multiple reports have been made concerning the importance of oxides and their dynamic nature during the eCO_2R. For example, Cheng *et al.*[46] described the nature of the active sites of OD-Cu electrocatalysts for the eCO_2R, while Bagchi *et al.*[47] reported on the time- and potential-dependent dynamic nature of an OD-PdIn nano-electrocatalyst. Similar observations concerning the dynamic and potential dependent nature of Sn oxides have been made for SnO_2-based electrocatalysts. Therefore, as evidenced here, we believe that after the improved initial adsorption of CO_2, due to the incorporation of nitrogen, the formation of surface-bound Sn carbonate is a key chemical intermediate in the eCO_2R towards FA on Sn-based electrodes [48]. Bocarsly *et al*. argued that prior to the eCO_2R, the presence of surface SnO_2 species enables the formation of Sn^{2+} oxyhydroxide through proton reduction. Subsequent reaction with CO_2 results in the formation of a surface-bound carbonate, which

is converted to HCOO⁻ via a two-electron and one proton transfer. After desorption of the final product, the Sn-based electrocatalyst is returned to its Sn^{2+} oxyhydroxide state [19,48]. This metastable Sn^{2+} oxyhydroxide has been proposed by multiple researchers as the active site for the eCO_2R towards FA on SnO_2-based electrodes. Analysis of the most predominant degradation mechanisms in the SnO_2-N-OMC electrocatalysts indeed confirms the importance of surface oxide species. It is important to note, however, that the proposed mechanism in figure 8 is the most plausible one, based on state-of-the-art literature, and that further experimental and theoretical studies, which fall out of the scope of this work, are required to confirm this. Previously, we proposed several mitigation strategies such as lowering the overpotential, co-electrolysis of CO_2 with low concentrations of oxygen (or other oxidants) or pulsed eCO_2R, to diminish the most detrimental degradation mechanism, the *in situ* SnO_2 reduction [26].
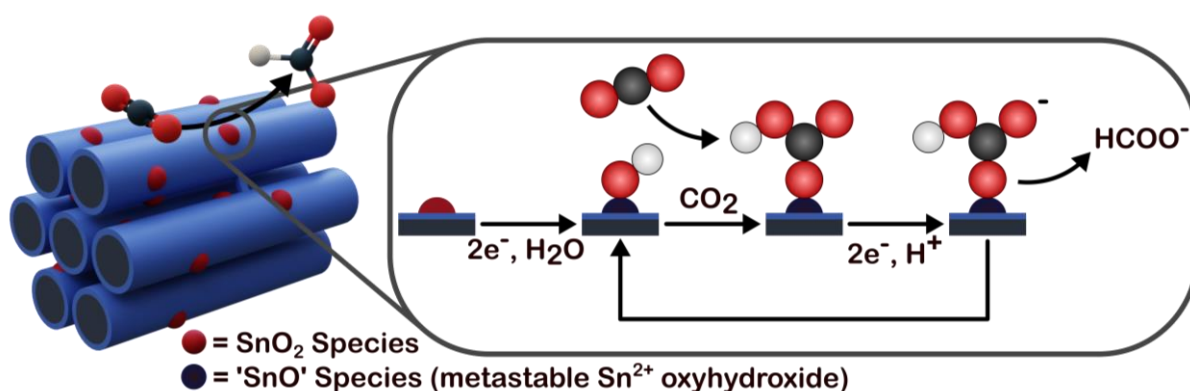
Figure 8. The most plausible reaction mechanism, based on state-of-the-art literature, for the eCO_2R towards formate on the SnO_2-N-OMC electrocatalysts, with Sn^{2+} oxyhydroxide as metastable active site [19,26,48].

4. Conclusion

In conclusion, we have demonstrated that including SnO_2 during the N-OMC synthesis has no significant effect on the N-OMC morphology, as long as part of the SnO_2 precursor is added simultaneously with the aniline. Including a SnO_2 precursor during different stages of the N-OMC synthesis resulted in a wide variety of SnO_2 species, ranging from large irregular SnO_2 species to differently sized SnO_2 nanoparticles and Sn-based atomic clusters. More importantly, we've successfully demonstrated that we are able to significantly increase the FE_{FA} utilizing a minimal amount of SnO_2, with the most selective morphologies being large irregular SnO_2 species and SnO_2 nanoparticles. Moreover, the SnO_2-N-OMC electrocatalysts require a low overpotential, due to the enhanced CO_2 adsorption capacity of the N-OMC support, for the selective (± 60%) conversion of CO_2 towards FA at the industrially relevant current density of 100 mA cm⁻², as such they perform better or at least as good as the current state-of-the-art. Finally, The long-term electrocatalytic stability and degradation pathways of the two best performing electrocatalysts (SnO_2-N-OMC (2) and SnO_2-N-OMC

(6)) were unraveled by combining 24 h chronopotentiometric experiments at an applied current density of 100 mA cm^{-2} with *ex situ* HAADF-STEM. While the FE_{FA} of SnO_2-N-OMC (6) decreased from 59% to 12% over the course of 24 h, the SnO_2-N-OMC (2) electrocatalyst displayed a smaller loss in FE_{FA} from 61% to 43%. This loss of selectivity was attributed to the *in situ* SnO_2 reduction, which in the case of the SnO_2-N-OMC (2) is offset to a greater degree by the pulverization of large SnO_2 species, revealing 'fresh' and selective SnO_2 active sites for the eCO_2R towards FA. While morphological stability of the Sn-based electrocatalyst is important in the long run, chemical stability to withstand *in situ* SnO_2 reduction appears to be more crucial for future Sn-based electrocatalysts as this directly correlates to a severe loss in selectivity. Our exploration of the interplay between SnO_2 and the N-OMC carbon capture medium support material revealed that an optimal combination of both the SnO_2 species and the N-OMC carbon capture medium could thus result in a synergistic effect for the eCO_2R towards FA, especially when utilization of the N-OMC support material and incorporation of the SnO_2 species is optimized to morphologically stabilize the SnO_2 active species. Hence, future research concerning Sn-based electrocatalysts should focus on improving the morphological and chemical stability in order to yield industrially relevant Sn-based electrocatalysts for the eCO_2R towards FA.

Supporting Information

eCO_2R electrolyser setup, physicochemical characterization SBA-15, BET surface area and pore size distribution plots of all (SnO_2-)N-OMC electrocatalysts, low angle XRD, HAADF-STEM images, overall average FE%, uncompensated potentials with varying CO_2/N_2 concentrations, state-of-the-art Sn-based and N-doped Sn-based electrocatalysts, XPS spectra and *ex-situ* wide angle XRD diffractograms of the as-synthesized SnO_2-N-OMC electrocatalysts before and after 24h of eCO_2R.

Acknowledgements

Conflicts of interest

There are no conflicts of interest to declare.

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Synergy or Antagonism? Exploring the Interplay of SnO$_2$ and an N-OMC Carbon Capture Medium for the Electrochemical CO$_2$ Reduction Towards Formate

Supporting Information

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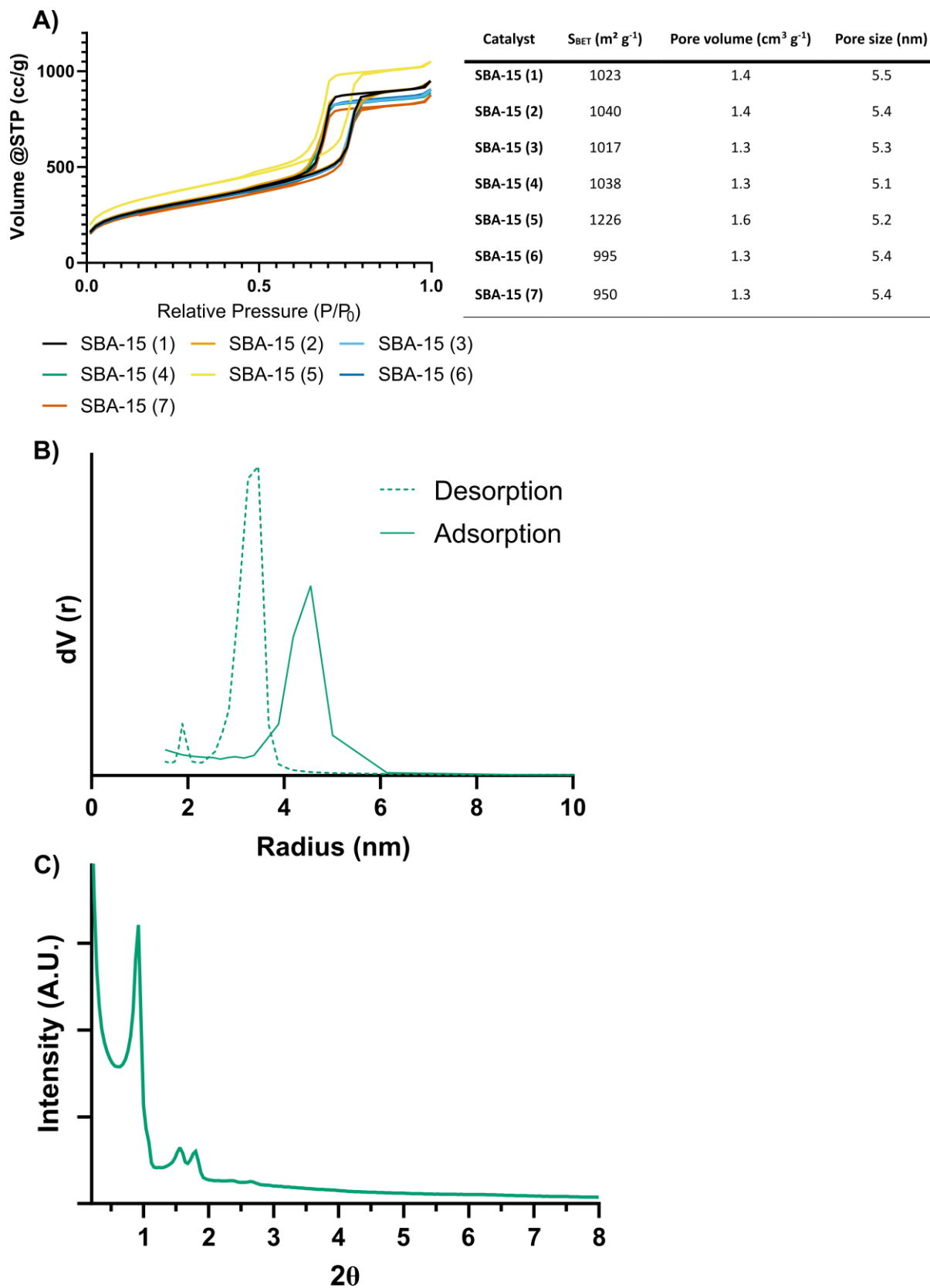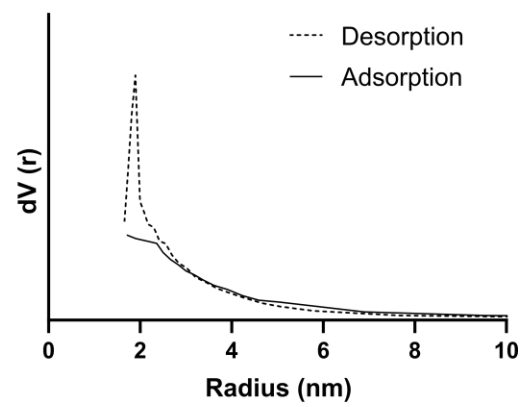
Figure S1. eCO$_2$R electrolyser setup

A)

Catalyst	S_{BET} (m² g⁻¹)	Pore volume (cm³ g⁻¹)	Pore size (nm)
SBA-15 (1)	1023	1.4	5.5
SBA-15 (2)	1040	1.4	5.4
SBA-15 (3)	1017	1.3	5.3
SBA-15 (4)	1038	1.3	5.1
SBA-15 (5)	1226	1.6	5.2
SBA-15 (6)	995	1.3	5.4
SBA-15 (7)	950	1.3	5.4

B)

C)

Figure S2. Physicochemical characterization SBA-15 with A) nitrogen adsorption-desorption isotherms of all SBA-15 samples, B) BJH pore size distribution of SBA-15 (4) and C) Low Angle XRD of SBA-15 (4)
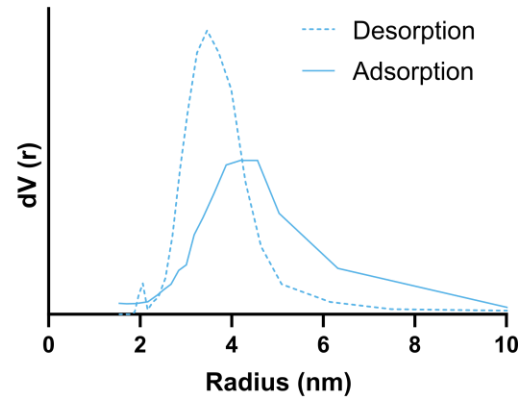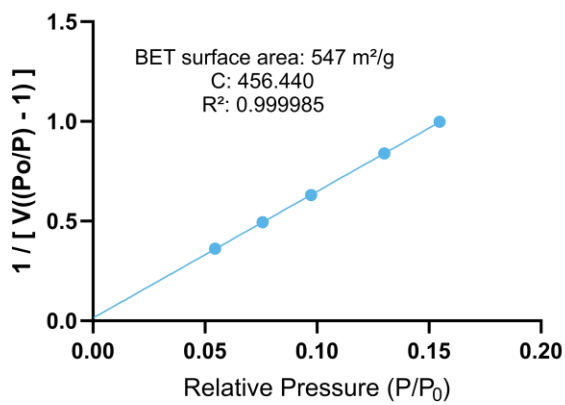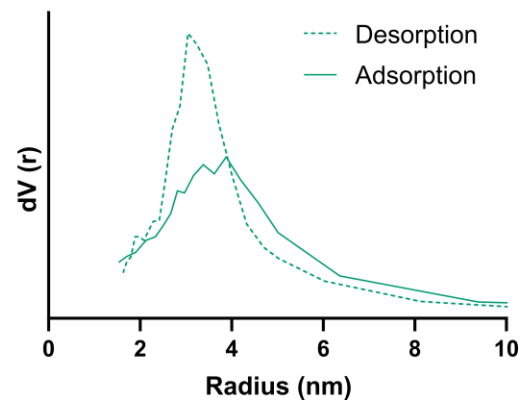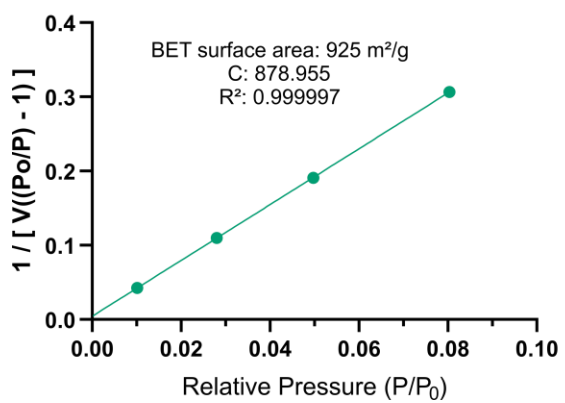
N-OMC (1)

BET surface area: 856 m²/g
C: 3472.991
R^2: 0.999840

- - - Desorption
—— Adsorption

SnO$_2$-N-OMC (1)

BET surface area: 952 m²/g
C: 812.067
R^2: 0.999995

- - - Desorption
—— Adsorption

SnO$_2$-N-OMC (2)

BET surface area: 547 m²/g
C: 456.440
R^2: 0.999985

- - - Desorption
—— Adsorption

SnO$_2$-N-OMC (3)

BET surface area: 925 m²/g
C: 878.955
R^2: 0.999997

- - - Desorption
—— Adsorption

SnO₂-N-OMC (4)

BET surface area: 722 m²/g
C: 1367.566
R²: 1.00000

SnO₂-N-OMC (5)

BET surface area: 689 m²/g
C: 1395.680
R²: 1.00000

SnO₂-N-OMC (6)

BET surface area: 767 m²/g
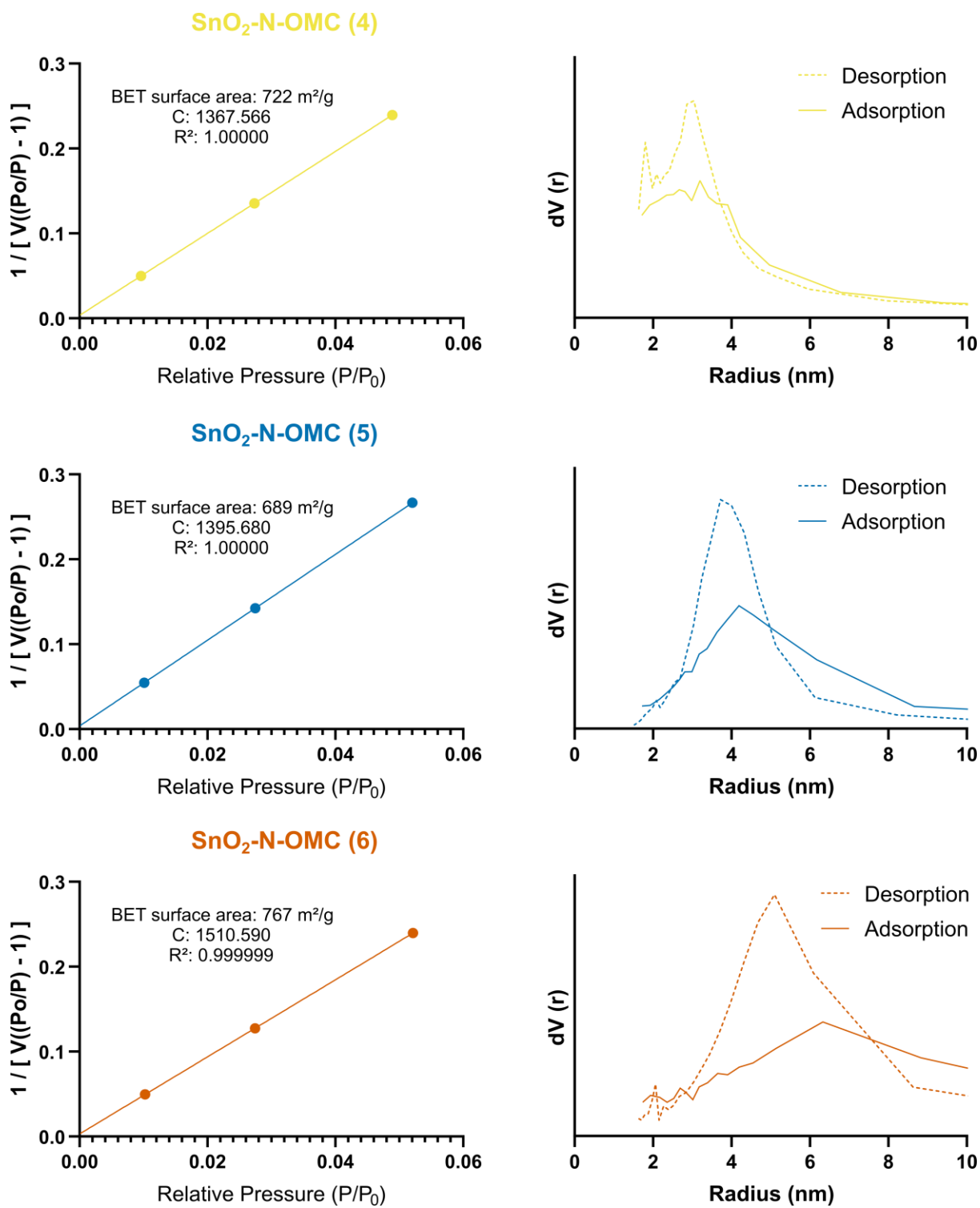C: 1510.590
R²: 0.999999

Figure S3. BET surface area and pore size distribution plots of all (SnO₂-)N-OMC electrocatalysts
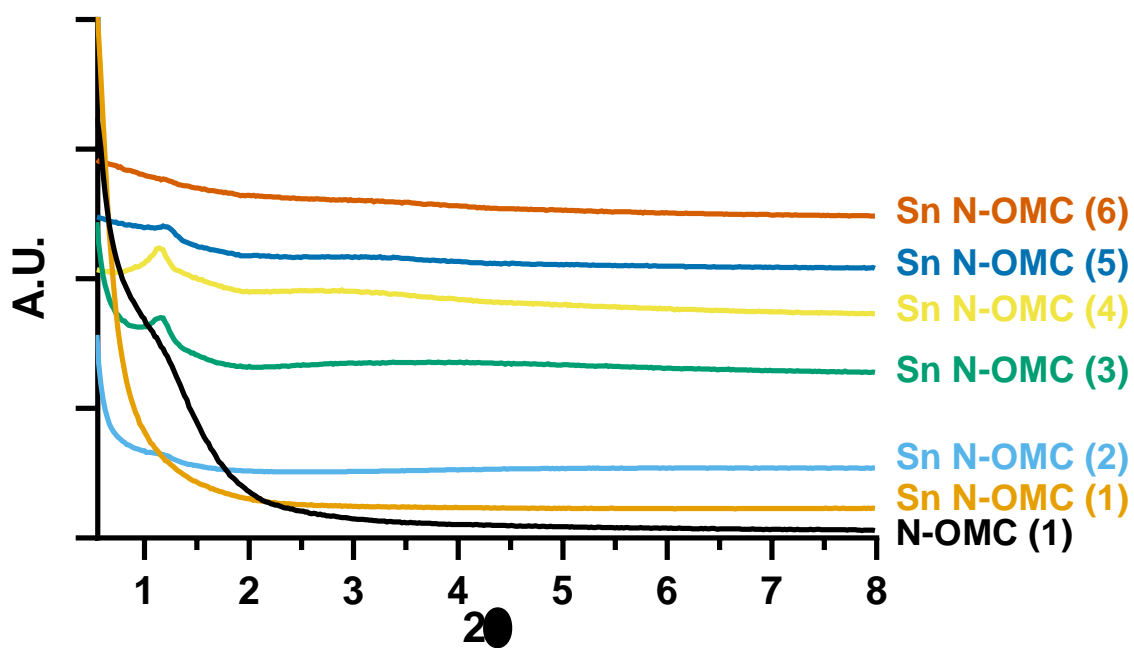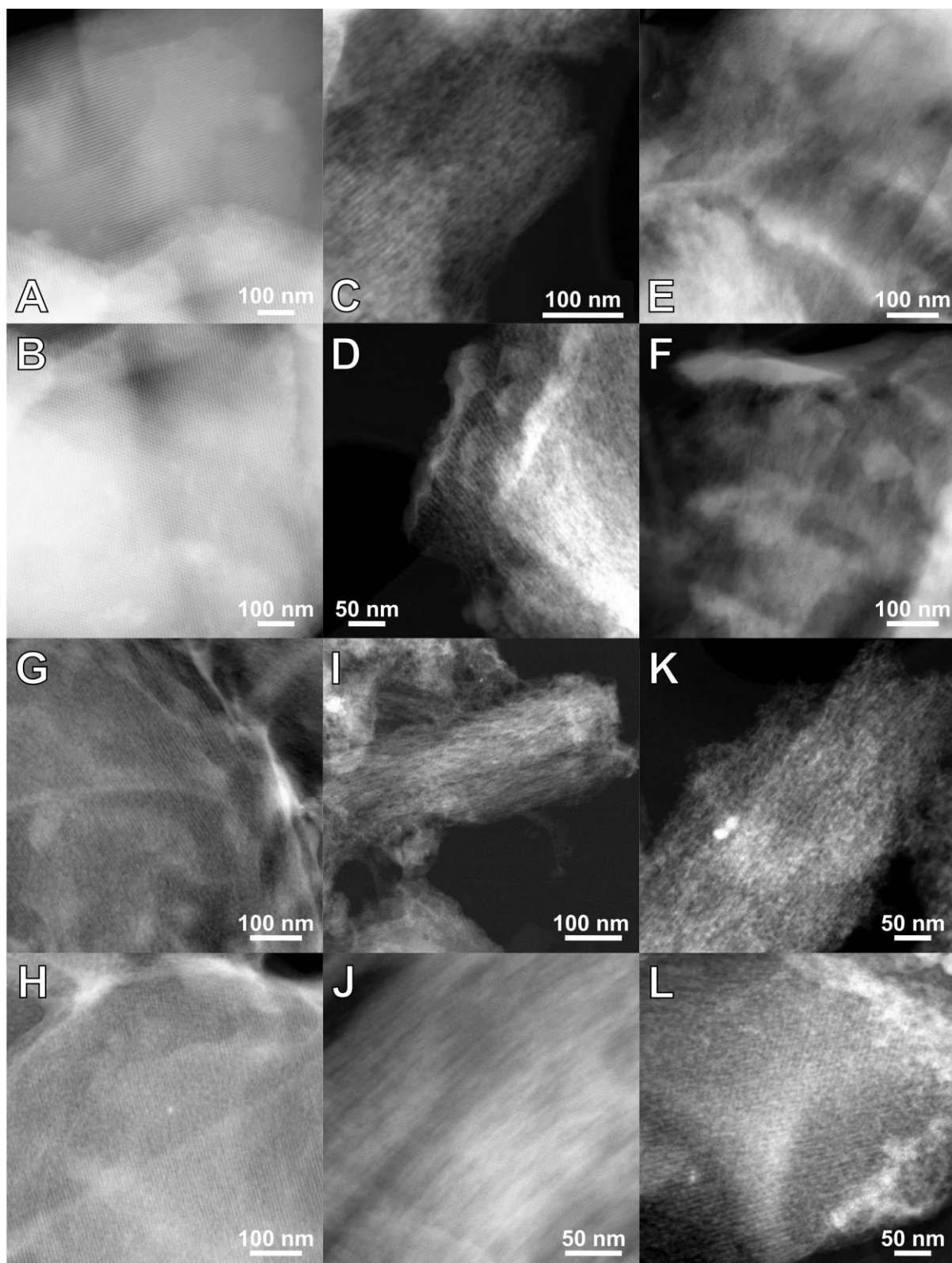
Figure S4. Low Angle XRD (SnO₂)-N-OMC electrocatalysts

Figure S5. HAADF STEM images of A, B) SBA-15; C, D) N-OMC (1); E, F) SnO$_2$-N-OMC (1); G, H) SnO$_2$-N-OMC (2); I, J) SnO$_2$-N-OMC (4) and K, L) SnO$_2$-N-OMC (6)
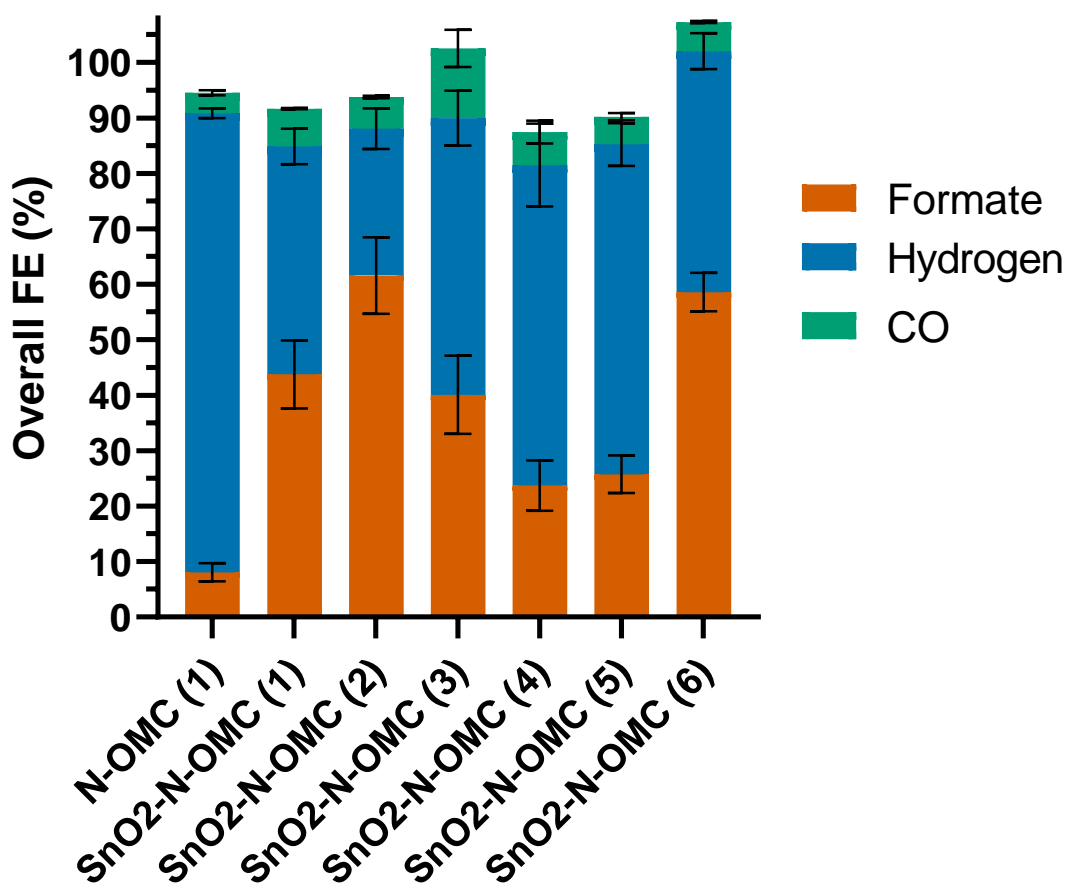
Figure S6. Overall average FE% for all seven electrocatalysts, measured at a constant current density of 100 mA cm^{-2} for 1 h.
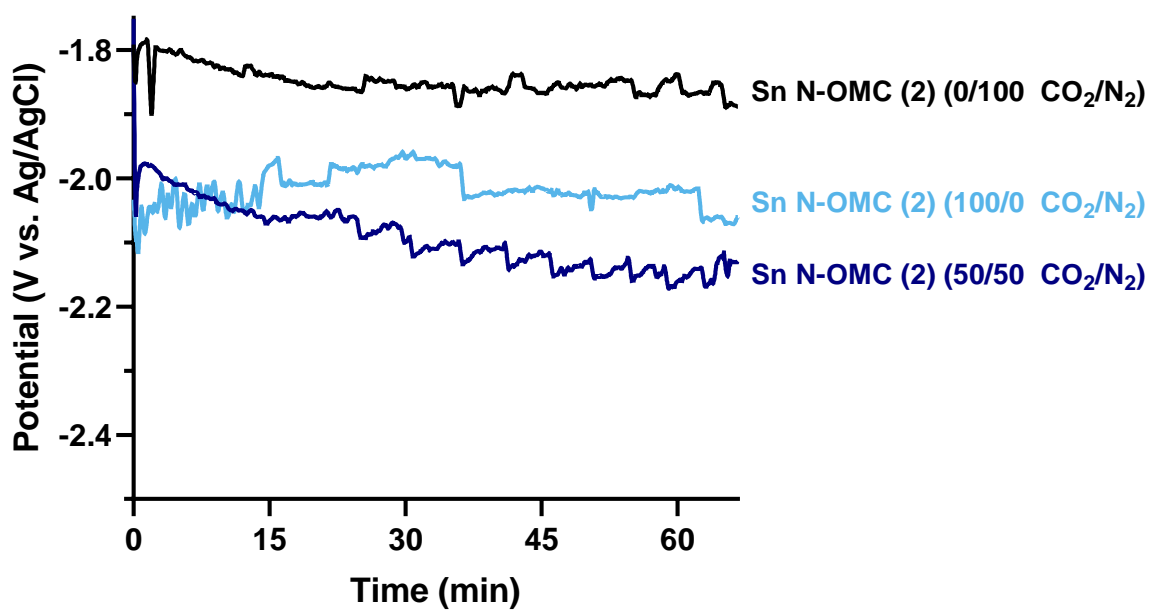

Figure S7. Uncompensated potential (V vs. Ag/AgCl) as a function of time at a constant current density of 100 mA cm^{-2} for 1 h, with varying CO$_2$/N$_2$ concentrations.

*Table S1. State-of-the-art Sn-based and **N-doped Sn-based** electrocatalysts*

| Catalyst	FE_{FA} (%)	Working Potential (V) vs. RHE	J (mA cm^{-2})	Stability (h)	Electrolyte	Ref.
$Bi_{0.1}Sn$*	95	-0.65	100	2400	1.0 M KHCO$_3$	[1]
Sn nanoparticles GDE*	94	-1.48	140	550	DI water	[2]
SnO$_2$ GDE*	70	-1.40	12	174	0.1 M KHCO$_3$	[3]
SnO$_2$/ɣ-Al$_2$O$_3$	65	-1.37	21.7	152	0.5 M KHCO$_3$	[4]
Bi-Sn/CF	96	-1.14	45	100	0.5 M KHCO$_3$	[5]
SnDT GDE*	62.5	-0.76	18.7	72	1.0 M KHCO$_3$	[6]
SnIn-3	84.6	-1.0	39	58	0.1 M KHCO$_3$	[7]
np-Sn/SnO$_2$	80	-1.1	16	58	0.5 M NaHCO$_3$	[8]
p-SnS$_x$	97	-1.0	15	50	0.1 M KHCO$_3$	[9]
CuSn$_3$	95	-0.5	33	50	0.1 M KHCO$_3$	[10]
$Sn_{0.80}Bi_{0.20}$@Bi-SnO$_x$*	>90	-0.88	20.9	50	0.5 M KHCO$_3$	[11]
Sn quantum sheets/GO	85	-1.16	21	50	0.1 M KHCO$_3$	[12]
SnO$_x$ NP-s*	81	-1.20	9.03	50	0.1 M KHCO$_3$	[13]
CuSn-10C	82	-1.0	18.9	42	0.1 M NaHCO$_3$	[14]
Sn(S)/Au	93	-0.75	55	40	0.1 M KHCO$_3$	[15]
Sn$_{2.7}$Cu GDE*	90	-0.55	243.1	40	1.0 M KOH	[16]
Pomegranate SnO$_2$@C	85	-0.70	100	24	0.5 M KHCO$_3$	[17]
Pomegranate SnO$_2$	80	-0.62	100	24	0.5 M KHCO$_3$	[17]
Commercial SnO$_2$ NPs	79	-0.50	100	24	0.5 M KHCO$_3$	[17]
SnO$_2$/CC	87	-0.97	50	24	0.5 M NaHCO$_3$	[18]
Ag$_{76}$Sn$_{24}$/SnO$_x$	80	-0.8	19.7	24	0.5 M NaHCO$_3$	[19]
Sn-N-C	70	/	100	24	0.5 M KHCO$_3$	[20]
Sn-CF1000	63	-0.8	16.6	24	0.5 M KHCO$_3$	[21]
SnO$_2$-N-OMC (2)*	**62**	**-0.54**	**100**	**24**	**0.5 M KHCO$_3$**	**This Work**
SnO$_2$-N-OMC (6)*	**58.6**	**-0.42**	**100**	**1**	**0.5 M KHCO$_3$**	**This Work**
SnO2⊃NC@EEG	81.2	-1.2	11	10	0.1 M KHCO$_3$	[22]
SnO2/N-MWCNTs	46	-0.9 V vs. Ag/AgCl	> 1	10	0.1 M KHCO$_3$	[23]
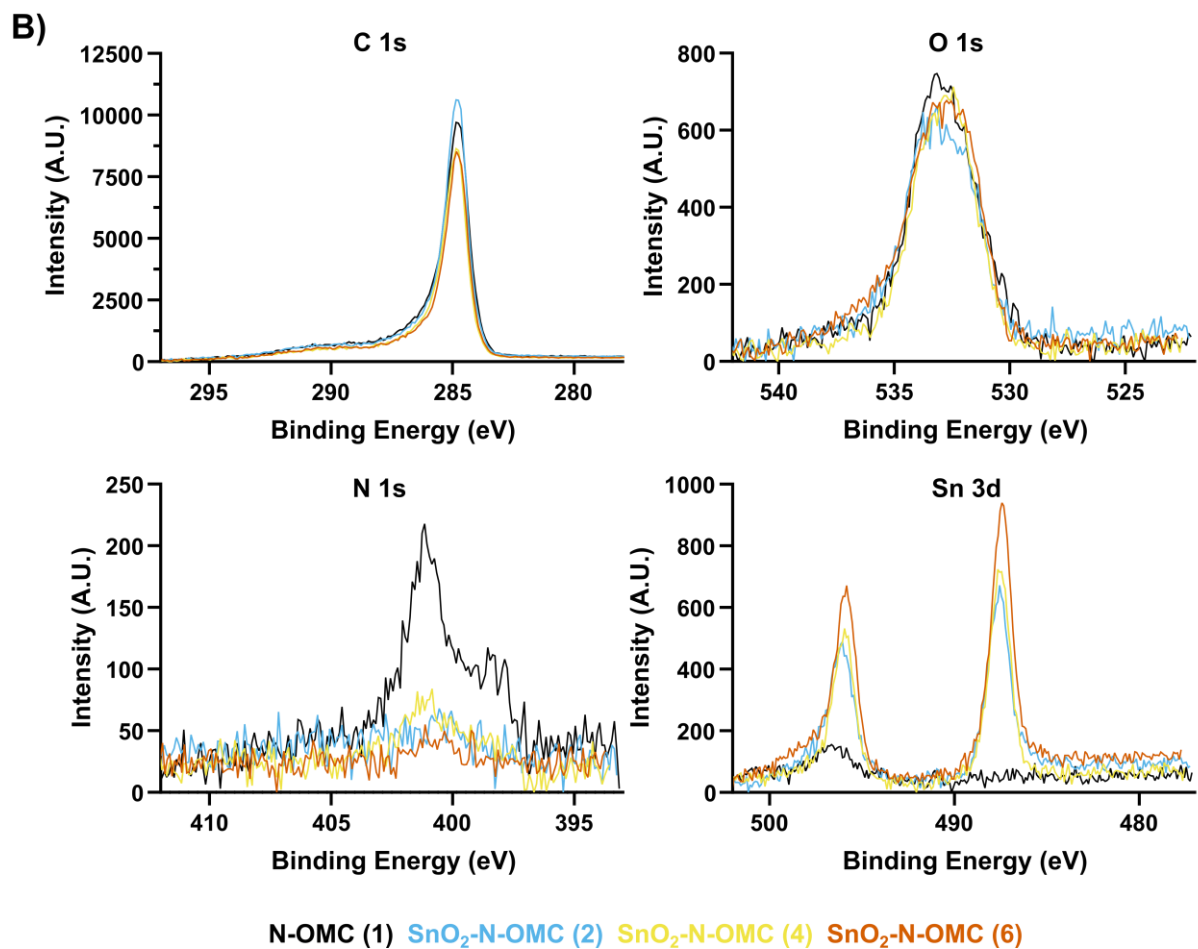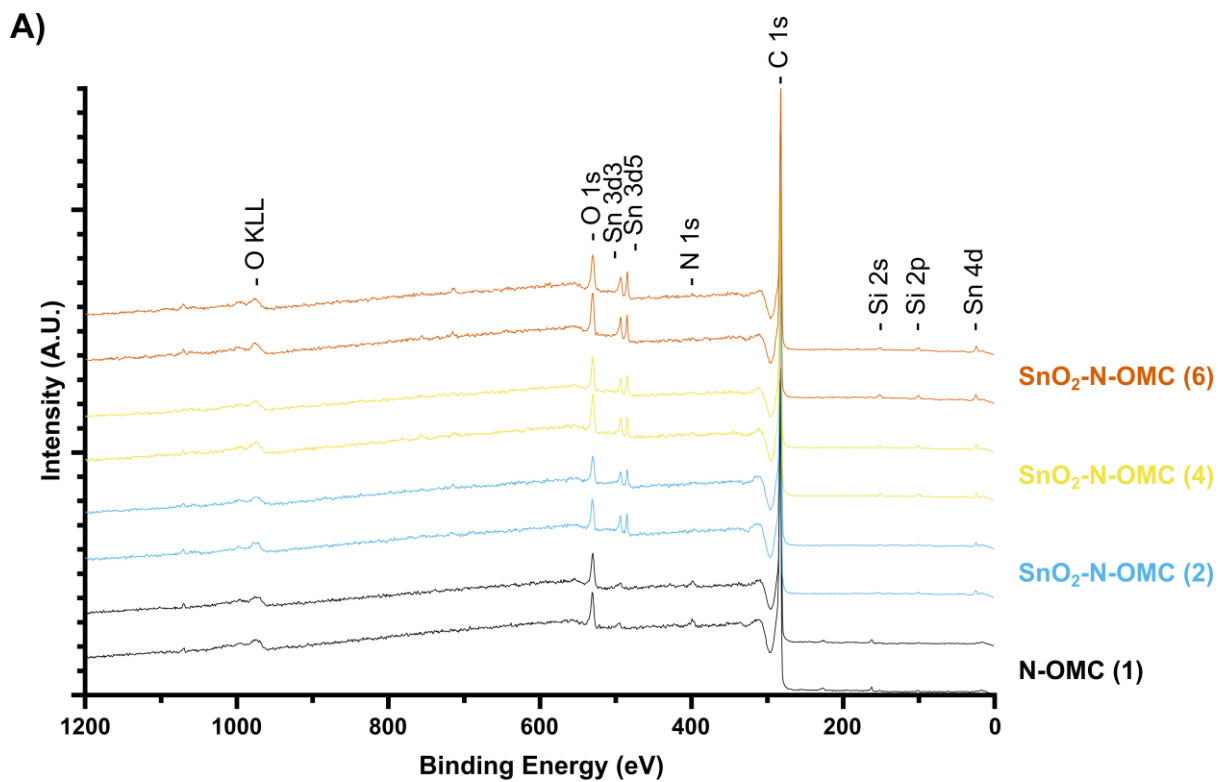
Figure S8. XPS spectra N-OMC (1), SnO$_2$-N-OMC (2), SnO$_2$-N-OMC (4) and SnO$_2$-N-OMC (6), with A) duplicate survey of all (Sn-)N-OMC electrocatalysts and B) high resolution spectra of C 1s, O 1s, N 1s and Sn 3d
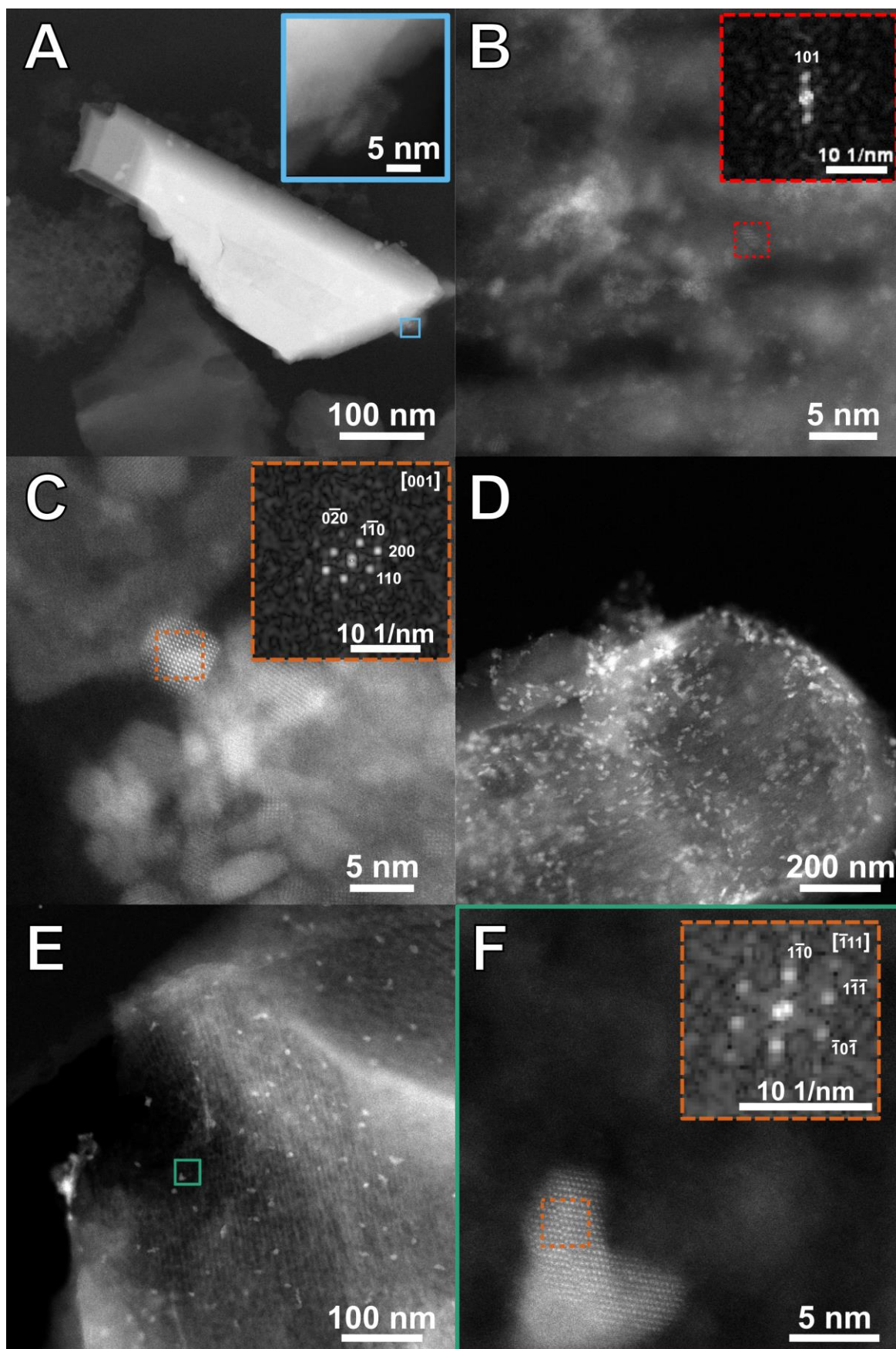
Figure S9. HAADF STEM images and the corresponding Fourier Transform (FT) patterns of A) an irregular large SnO_2 species and B) atomically dispersed species, presumed to be Sn-based and C) SnO_2 nanoparticles in SnO_2-N-OMC (2); D, E and F) SnO_2 nanoparticles in SnO_2-N-OMC (6).
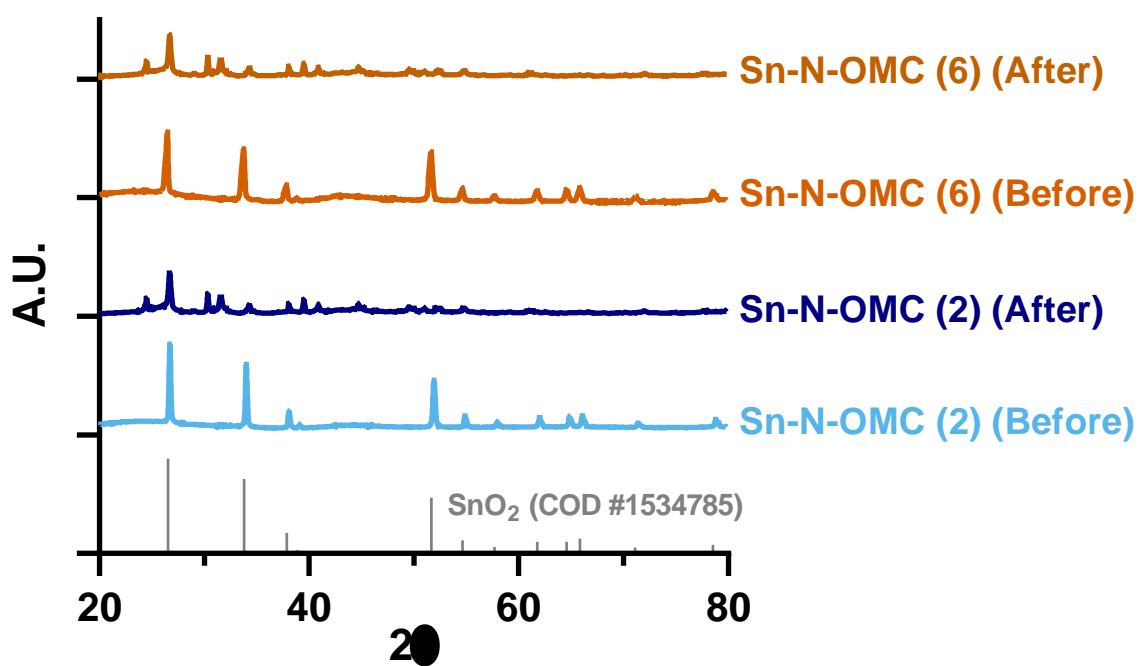
Figure S10. Wide angle X-ray diffractogram of the as-synthesized SnO$_2$-N-OMC electrocatalysts, before and after 24h of eCO$_2$R, compared with the Crystallography Open Database (COD) #1534785 for tetragonal SnO$_2$.

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