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Chlorine-modulated tin oxide as an efficient catalyst toward carbon dioxide electrochemical reduction

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ABSTRACT

Electrochemical conversion of CO₂ into value-added chemicals such as formic acid shows promise in carbon neutralization for carbon-intensive manufacturing industry, such as iron-steel industry or ammonia production industry. However, low product selectivity and competitive hydrogen evolution over Sn-based catalysts severely lower the energy efficiency of this process and increase the cost of downstream product separation. In this work, we demonstrated a facile strategy to improve conversion efficiency of CO₂ at a relatively low overpotential by incorporating chlorine element into tin oxide. We found that the less electronegative chlorine than oxygen could lower the valence of surface Sn to an optimal level for CO₂ reduction. As a result, the chlorine-modulated Sn showed an overall CO₂ conversion Faradaic efficiency of 82.9% at -0.783V vs RHE, over 43% higher than those over commercial Sn foil and SnO₂-derived nanoparticles (<100nm).

INTRODUCTION

Coupled with low-carbon emission power such as wind or solar, electrochemical conversion of waste CO₂ emitted from manufacturing processes, such as iron-steel making or ammonia production into value-added chemicals, provides a promising route to reduce CO₂ emissions in a cost-effective way (Graves, Ebbesen et al. 2011, Otto, Grube et al. 2015, Wang, Liu et al. 2018). However, one of the challenges that limit the deployment of CO₂ conversion technologies is its poor product selectivity to desired products (e.g. CO, CH₄, methanol, C₂H₄) due to the competing hydrogen evolution reaction (HER) and the wide spectrum of products from CO₂ reduction reaction (CO₂RR). Poor product selectivity leads to a low energy efficiency for CO₂ conversion and unacceptable operating cost for downstream product separation (Greenblatt, Miller et al. 2018).

Formic acid could be an attractive target product for CO₂RR because it has a relatively high commercial value (~1.2\$ kg⁻¹) and only requires a low energy consumption. (Agarwal 2011) Tin (Sn) metal-based catalysts are shown to be effective and selective for CO₂RR to formic acid or formate (Zhang, Kang et al. 2014, Li, Chen et al. 2017, Zheng, De Luna et al. 2017, Zhang, Zhang et al. 2019), and Sn is a low-cost material. However, Sn catalysts still provide low CO₂RR conversion efficiency particularly at a low overpotential. To circumvent this challenge, extensive efforts have been devoted to further optimize the Sn-based catalysts, including: (1) reduction of Sn catalyst

particle size to nanoparticles or nanosheets (Zhang, Zhang et al. 2019); (2) alloying with metals such as Pb(Choi, Jeong et al. 2016), Au(Ismail, Samu et al. 2019), Cu(Zheng, Ji et al. 2019), and S(Zheng, De Luna et al. 2017); (3)oxide derivation(Chen and Kanan 2012, Pander, Baruch et al. 2016, Daiyan, Lu et al. 2018, Ge, Gu et al. 2018).

Valence of Sn plays an important role in the selective CO₂RR to formate. Previous experimental studies revealed that CO₂RR to formate over Sn likely proceeds via a surface-bound carbonate (*OCHO intermediate) interacting with the Sn(II) oxyhydroxide species(Baruch, Pander et al. 2015). Dutta et al.(Dutta, Kuzume et al. 2015) observed a strong correlation between Sn valence and formate selectivity, and reported that an optimal formate selectivity can be achieved at the transition between SnO₂ to Sn metal.

The hypothesis we tested in this study is that adding chlorine, which has an lower electronegativity of 3.16 compared to oxygen (3.44) (Allred 1961), to Sn-based catalysts could be beneficial for CO₂RR to formate.

We synthesized a novel SnOxCly catalyst through a facile synthesis method, and compared its CO₂RR performance with a commercial Sn foil and SnO₂ nanoparticles (<100nm). We found that the SnOxCly showed a significant improvement in formate production and effective suppression of unwanted HER at more positive potential as compared to other Sn-based analogues. This improvement could be a result of the presence of Cl ions, which modulate the valence of Sn at low potentials towards a better catalytic activity.

EXPERIMENTAL SECTION

Catalyst preparation

To prepare the SnOxCly sample, we added 2.26g of SnCl₂·2H₂O (≥99.99%, Sigma Aldrich) precursor into 50mL deionized water stirred by a magnetic stirrer at a stirring rate of 400 rpm. After stirring for 24 h, we collected the solid product from the solution through centrifugation. The product was washed at least three times with deionized water under sonication for at least 20min each time, once with ethanol, and finally dried under vacuum at room temperature.

Electrode preparation

The catalysts were loaded onto a Toray 060 carbon paper (FuelCellStore) substrate to form the cathode electrodes. We had cleaned the carbon paper ultrasonically in 0.1M HCl, deionized water and isopropanol and then rinsed it in deionized water again, and finally dried the carbon paper in the air. We dispersed 10mg of the catalyst powder (i.e. SnOxCly and SnO₂) and 10mg carbon black (Super P Conductive, Alfa Aesar) in 100μL Nafion perfluorinated resin solution (5 wt.%, Sigma Aldrich) and 500μL isopropanol (≥99.7%, Sigma-Aldrich) before sonicating it for 1h to form a uniform catalyst ink. Afterwards, we painted the ink on carbon paper, and the total loading of the solid was controlled to be approximately 1 mg cm⁻². We prepared the Sn foil electrode (99.99%, Sigma Aldrich) by polishing the Sn foil with diamond and alumina polishing pad (PK-3 polishing kit from ALS Japan), washing Sn foil in deionized water for at least 30min, and electrochemically polishing the Sn foil for another 30 min in a CO₂-saturated 0.5M KHCO₃.

Electrochemical measurement

A custom-designed gas-tight H-cell with anode and cathode chambers separated by a proton exchange membrane cell (Nafion 117, FuelCellStore) was used to evaluate CO₂RR performance of the targeted samples. The experiment was carried out in a three-electrode system, and reference electrode is the Ag|AgCl (3M NaCl) (from ALS Japan) and the counter electrode is a graphite rod. Cathode and anode compartment contained 70mL and 30mL of 0.5M KHCO₃(99.5%, Sigma-Aldrich) electrolyte, respectively. Before measurement, the electrolyte was saturated with CO₂ gas (99.999%, Supagas Australia) for at least 30 minutes, reaching a measured pH value of 7.45. During the experiment, 30 sccm CO₂ gas was bubbled into the catholyte solution stirred at 500rpm. All the electrochemical measurements were performed by a potentiostat (Autolab 302N). The experiment was conducted at room temperature and ambient pressure. We in-situ measured the temperature and pH of the electrolyte in the cathode chamber during all the electrochemical measurements using Metrohm LL Unitrode PT1000 (F/2mm).

All potentials applied were converted to reversible hydrogen electrode (RHE) by the following equation:

$$E_{RHE} = E_{Ag|AgCl} + \frac{2.303 \times R \times T}{F} \times pH + 0.195$$

Where T is the measured temperature (K) of electrolyte, and pH is the measured pH, F is the Faradaic constant (96485 C mol⁻¹), and R is the ideal gas constant (8.314 J mol⁻¹ K⁻¹). Cyclic Chromatography (CV) was performed at a scan rate of 10 mV/s. Chrono Amperometry and Electrochemical Impedance Spectroscopy were performed under a range of applied potentials.

Product analysis

The gas products were measured by online gas chromatography (Shimadzu GC-2030) equipped with a thermal conductivity detector (TCD) and flame ionization detector (FID) with Ar as the carrier gas, hydrogen as the fuel gas, and zero air as the balance gas. Prior to the experiment, calibrations were performed using a series of standard hydrogen and CO mixtures with known concentration balanced with Ar. The faradaic efficiency (FE) of CO was calculated as follows:

$$FE(\%) = \frac{Q_{product}}{Q_{total}} \times 100\% = \frac{P \times v \times c_{product} \times F \times N}{R \times T \times j} \times 100\%$$

Where $v=30$ sccm is the volumetric flow rate of CO₂, $c_{product}$ is the measured volume concentration of product in 1 mL sample loop based on the calibration results of the standard gas, P is atmospheric pressure. F is the faradaic constant (96485 C mol⁻¹). N is the number of electrons required to transfer to form one mole of H₂ or CO, so $N = 2$. j is the current recorded by potentiostat.

The liquid product was regularly collected after each electrochemical measurement. We used ¹H-nuclear magnetic resonance (NMR) analysis to measure the concentration of the formate in the liquid product and calculated the Faradaic efficiency of the formate. The NMR testing samples were prepared prior to the NMR test by mixing 400uL liquid sample and 200uL deuterium oxide mixed with 0.05 vol% dimethyl sulfoxide (DMSO, ≥ 99%, Sigma Aldrich) as the internal reference. The FE of formate was calculated by following equation

$$FE(\%) = \frac{Q_{HCOO^-}}{Q_{total}} \times 100\% = \frac{n_{HCOO^-} \times N \times F}{Q_{total}} \times 100\%$$

Where n_{HCOO^-} is the number of the moles of formate in the cathodic compartment calculated from the NMR results.

Materials Characterization

The crystal structures of the samples were characterized by X-ray diffraction with Cu-Kα as the radiation source. We studied the morphology of the samples through scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Energy-dispersive X-ray spectroscopy (EDS) of TEM was performed to analyze the concentration of composition in the bulk of the samples, while the composition and chemistry of the sample surface was investigated by using X-ray photoelectron spectroscopy (XPS).

RESULT AND DISCUSSION

The X-ray diffraction (XRD) pattern of the synthesized sample at room temperature was shown in Figure 1a. The diffraction peaks are very broad, indicating the formation of nano-size particles of SnOxCly. By comparing with the XRD patterns sourced from the PDF-4 2019 database, we found that the sample consists of phases corresponding to SnO₂ and SnO and possibly Sn₄(OH)₆Cl₂ phases. The high-resolution TEM image, as shown in Figure 1b, confirmed that the SnOxCly particles are in fact agglomerates of small crystallites that are within ~5nm in diameter. This is consistent with the broadened diffraction peaks as observed in XRD pattern presented in Figure 1a. Additionally, the TEM-EDS elemental mapping (Figure 1c-1e) shows that the compositions of the SnOxCly sample,

including Sn, O, and Cl, are uniformly dispersed in the SnOxCly particles, which provides further evidence of our successful incorporation of chlorine element into the tin oxide. Further quantification analysis of EDS mapping suggested that SnOxCly has 60atom% of Sn, 37.2atom% O and 7.2atom% Cl.

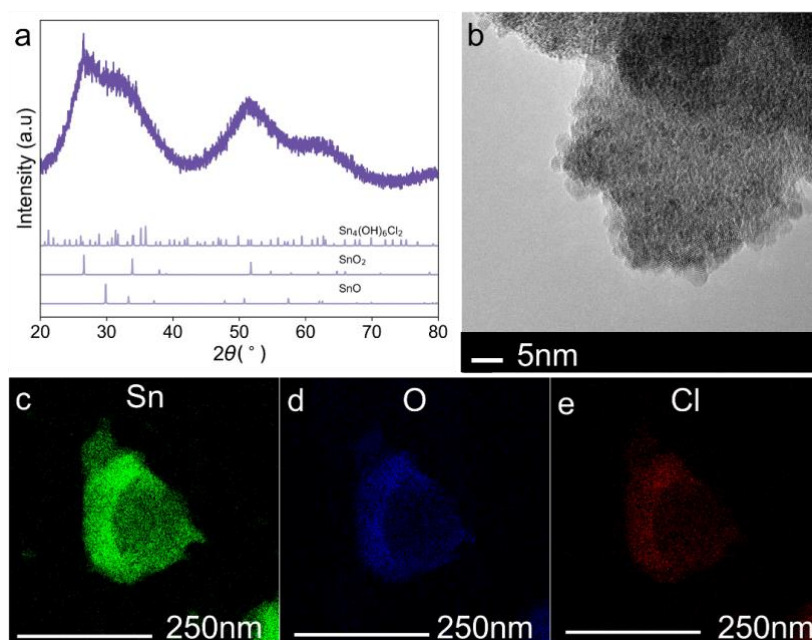


Figure 1 (a) X-ray diffraction of SnOxCly powder at room temperature versus $\text{Sn}_4(\text{OH})_6\text{Cl}_2$ (#00-015-0676), SnO_2 (#00-021-1250), and SnO (#00-006-0395) standard powder diffraction from database PDF-4 2019. (b) High resolution transmission electron micrograph (TEM) of SnOxCly, and elemental mapping of (c) Sn, (d) O, and (e) Cl element through TEM energy dispersive X-ray spectroscopy.

The high-magnification of scanning electron micrographs (SEM), as shown in Figure 2a, revealed that the as-prepared SnOxCly particles are micron-size agglomerates that are made of nano-size particles, as confirmed in Figure 1b. In comparison, the particle size of commercial SnO_2 nanoparticles (<100nm) are much smaller than as-prepared sample. (Figure 2c). SEM images in low magnification of SnOxCly and SnO_2 nanoparticles further confirm the smaller size of SnO_2 than SnOxCly. A small size of catalyst could strengthen its interactions with CO_2RR intermediates (Zhu, Michalsky et al. 2013), which could lead to deeper CO_2RR products such as CO than formate, and also may benefit the overall reaction rate due to a higher specific surface area.

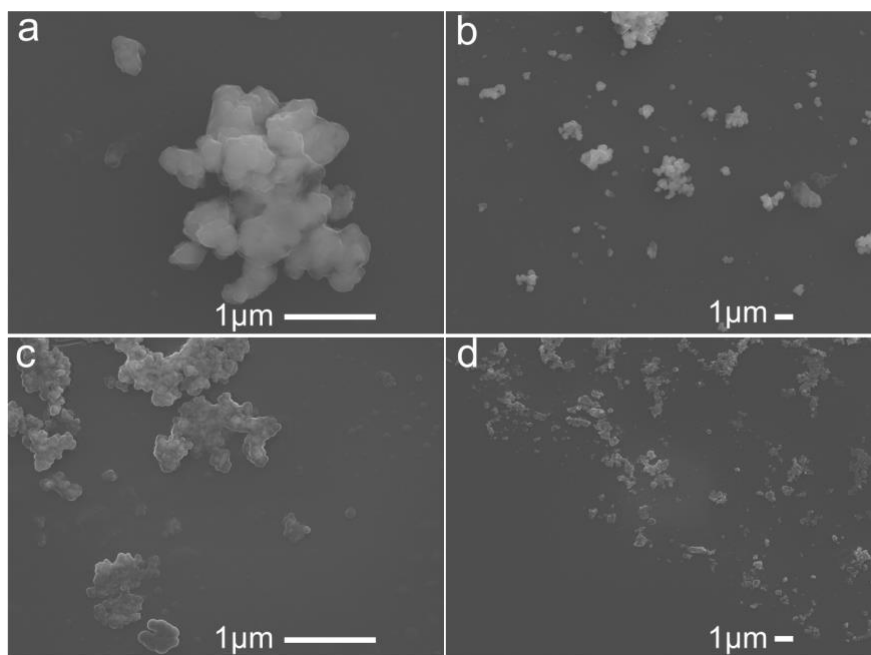


Figure 2 Scanning electron micrograph (SEM) of SnO_xCl_y particles in (a) high magnification and (b) low magnification; SEM of commercial SnO_2 nano-particles in (c) high magnification and (d) low magnification.

High resolution of X-ray photoelectron spectroscopy (XPS) measurement was performed to investigate surface chemistry of SnO_xCl_y and commercial SnO_2 nanoparticles before and after cathodic treatment in CO_2 . As shown in Figure 3, the Sn $3d_{5/2}$ peak of SnO_xCl_y with no treatment can be deconvoluted into two major peaks: one peak at $\sim 486.3\text{eV}$ that likely corresponds to Sn^{2+} (Jiménez, Fernández et al. 1996), and another at $\sim 488.3\text{eV}$ can be likely assigned to Sn species interacting with Cl. The commercial SnO_2 has the major deconvoluted peak at $\sim 486.6\text{eV}$ that is associated with Sn^{4+} (Li, Chen et al. 2017), which is as expected for the SnO_2 nanoparticle. Generally, SnO_xCl_y shows a lower valence at the surface than SnO_2 .

We also treated samples as electrodes in a CO_2 -saturated 0.5M KHCO_3 at a constant potential of -0.784V vs RHE and -0.984V vs RHE for 30min. The electrodes were prepared by painting the samples with Nafion ionomer as the binder onto the carbon papers. After the electrochemical treatment of all the samples, which were carried out at the same day, we quickly washed the electrode with deionized water, dried the electrode, and transferred directly for XPS measurement in vials that were filled with inert gas. These procedures are to prevent serious oxidation of Sn species in air, though potential oxidation of Sn during sample manipulation for XPS measurement. As presented in Figure 3, we found that generally at a more negative potential (-0.984V vs RHE), the XPS peaks of Sn $3d_{5/2}$ shifted to a lower binding energy, indicating the reduction of Sn species at more negative potential. It is interesting to note that the surface Sn species at SnO_xCl_y show a lower valence state than at SnO_2 , as evidenced by the observed higher proportion of metallic Sn peak at $\sim 484.7\text{eV}$ (Willems, Van De Vondel et al. 1979) and Sn^{2+} . Because we treated SnO_xCl_y prior to SnO_2 treatment, so SnO_xCl_y samples should be more oxidized by air than SnO_2 sample due to the longer time exposure to air. Therefore, we could rule out the impacts from the testing sequence but confirm our hypothesis that the incorporation of less electronegative chlorine could stabilize a relative low valence of Sn, which is in a CO_2RR -beneficial ‘transition-state’ from Sn^{4+} to Sn^{2+} .

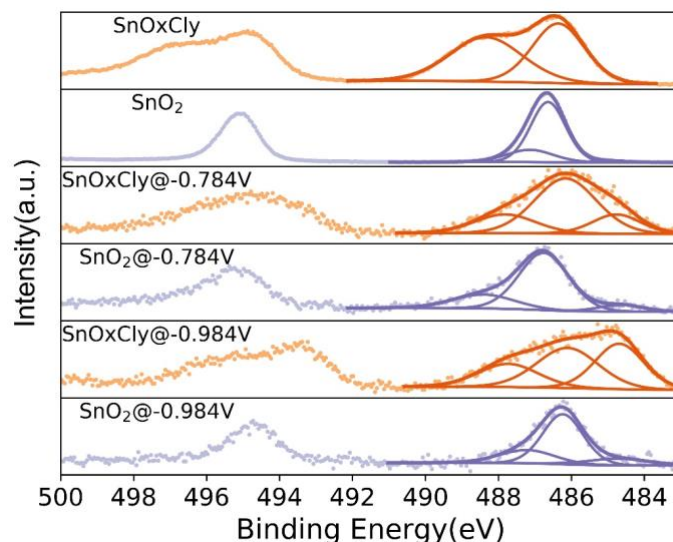


Figure 3 X-ray photoelectron spectra (XPS) of SnOxCly and commercial SnO₂ nanoparticles without electrochemical treatment and treated at -0.784V and -0.984V vs RHE.

To investigate the CO₂RR performance of the targeted samples, herein, we first studied the electrode substrate (i.e. carbon paper) and 0.5mg cm⁻² carbon black loaded on the carbon paper through cyclic voltammetry (CV) analysis in 0.5M KHCO₃ saturated with Ar or CO₂. These two electrodes showed very low current density and negligible CO₂RR activity as evidenced by the even lower current density in CO₂ than in Ar. (Inset in Figure 4a) Figure 4a shows CV of the electrode consisting of 0.5mg cm⁻² carbon black and 0.5mg cm⁻² SnOxCly. The commercial Sn foil and SnO₂ nanoparticles (<100nm) were also tested for comparison. Note that it is more appropriate to use SnO₂-derived and SnOxCly-derived catalysts to describe the samples for CO₂RR test because they were likely subject to reduction under the CO₂RR conditions. However, we still used their original names in Figure 4 for simplification. Before evaluating the performance of Sn foil, the Sn foil was thoroughly polished, cleaned, and electrochemically reduced in an attempt to achieve a clean surface. As shown in Figure 4a, only SnO₂-derived catalyst exhibited a relatively high overall current density at a potential more positive than -1.0V. Although at a more negative potential (<-1.0V), both SnOxCly-derived and Sn foil have a slightly higher current density than SnO₂, we believe their differences in overall current density are negligible. Therefore, the particle size of Sn-based catalyst or compositions seems not effective to affect the overall current density of the electrode.

As aforementioned, the product selectivity is an important factor to determine the energy efficiency and posit product separation complexity for the CO₂RR. Therefore, we evaluated the Faradaic efficiency (FE) of formate (HCOO⁻), CO, and H₂ over these samples during the electrochemical reduction. The results are presented in Figure 4b-4d. The overall FE of formate, CO and H₂ for all tested samples are close to 100%, and the formate is the major product for the three Sn-based electrodes, and the synthesized SnOxCly outperforms its analogues in the selectivity of CO₂ conversion particularly at more positive potential (i.e lower overpotential). For example, at -0.784V vs RHE (i.e. low overpotential), the SnOxCly exhibits a higher FE(HCOO⁻) of 63%, 0.3 and 0.9 times higher than the commercial Sn foil (FE(HCOO⁻)=47%) and SnO₂-derived catalysts (FE(HCOO⁻)=33%), respectively. At the same potential, the total FE for CO₂ conversion is ~82.9% for SnOxCly-derived catalyst, ~57.8% for Sn foil, and ~50.6% for SnO₂-derived catalyst, further demonstrating a remarkable improvement of CO₂RR selectivity at low overpotential due to the incorporation of chlorine element. The unwanted HER was more effectively suppressed for the developed SnOxCly sample, as compared to the other two Sn analogues. (Figure 4d) As reported elsewhere(Dutta, Kuzume et al. 2015), the transition state of Sn from SnO₂ to metallic Sn is optimal to produce HCOO⁻. The higher FE(HCOO⁻) for SnOxCly could be explained by the observed relatively low valence of Sn species at the surface as imparted by the introduction of less electronegative chlorine ions than oxygen. (Figure 3) When the potential is below -0.984V, the FE (HCOO⁻) is nearly the same for all the three samples at FE(HCOO⁻) above 70%, indicating a similar catalytic properties of Sn catalysts to metallic Sn, and chlorine or oxygen no longer contributes to the catalysis over Sn surface.

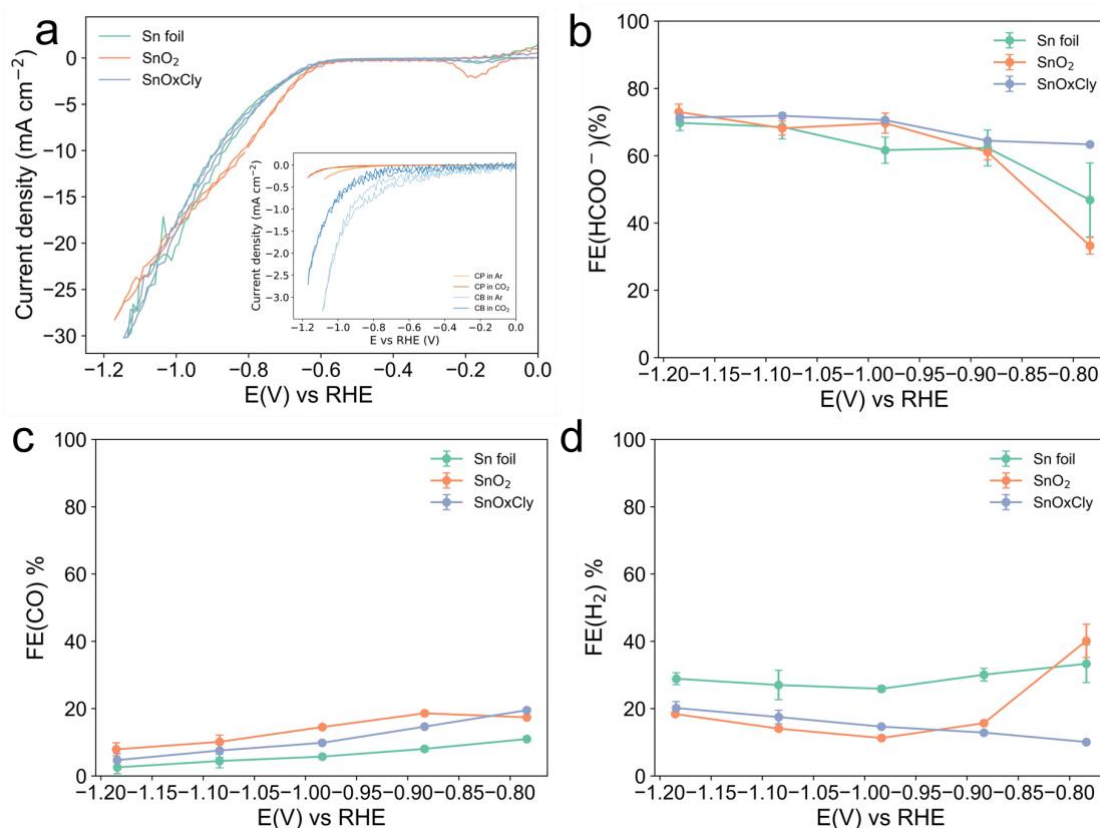


Figure 4 (a) Cyclic voltammograms (CV) of SnOxCly, SnO₂ and Sn foil in CO₂-saturated 0.5M KHCO₃, and the inset in (a) shows a comparison of CV curves for bare carbon paper and carbon paper loaded with 0.5mg cm⁻¹ carbon black in Ar- and CO₂-saturated 0.5M KHCO₃. Faradaic efficiency of (b) formate (c) CO and (d) H₂ as a function of potentials over Sn foil, SnO₂, SnOxCly samples in CO₂-saturated 0.5M KHCO₃ aqueous electrolyte. The error bar for gas product analysis was estimated by repeating at least three times over the gas detections. The error bar for formate detection was calculated through error propagation from the uncertainty of the nuclear magnetic resonance, as estimated by test three different mixtures of deuterium oxide with the same liquid solutions.

CONCLUSIONS

We introduced chlorine element into tin oxide through a facile room-temperature synthesis route to obtain SnOxCly particles as active catalysts for CO₂ electrochemical reduction. We demonstrated that the SnOxCly catalyst enhanced CO₂RR conversion (total FE of CO₂RR=82.9%) by a factor above 43%, and formate selectivity by a factor above 30%, as compared to commercial Sn foil and SnO₂-derived nanoparticles (<100nm) at a potential of -0.783V vs RHE. This significant improvement of CO₂RR at low overpotential arises from the incorporation of chlorine element that is less electronegative than oxygen. Through analyzing the surface chemistry of Sn, we demonstrated that chlorine element could lower the valence of Sn species at surface to an optimal level that contributes to the observed efficient conversion of CO₂ at relatively low potential.

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BIOGRAPHY

Peiyao Zhao

Ms Peiyao Zhao is a 4th year undergraduate student from China University of Petroleum (East China) and a visiting scholar at UQ. She is currently with HBIS-UQ ICSS centre to develop cost-effective catalysts for CO₂ electrochemical reduction under the supervision of Dr. Thomas E. Rufford and Dr. Mengran Li. After finishing her research work at UQ, she will come back to China and further pursue a graduate degree in the US.

Mengran Li

Dr. Mengran Li received his BEng in 2012 from Tianjin University and his PhD in 2016 from UQ. His current research is mainly focused on advancing electrochemistry-based technologies to circumvent formidable challenges in energy and environment sustainability through material innovation and process optimization. His research has led to 13 peer-reviewed international journal papers, including one paper published as the first author in *Nature Communications*. He now is working with the Innovation Centre for Sustainable Steel and HBIS Group to develop economically viable CO₂ conversion technologies to mitigate carbon emission from carbon-intensive iron-steel making processes.

Sahil Garg

Sahil Garg is a second year PhD student in chemical engineering at the University of Queensland, Australia. His research focuses on investigating electrolytes to understand their interaction with catalysts for enhanced CO₂ electrochemical reduction performance. In 2012, he did his B.Tech. from Indian Institute of Technology Gandhinagar, India, and afterwards, completed his M.S. in 2016 from Universiti Teknologi Petronas, Malaysia with a focus on developing solvents for CO₂ capture. Currently, he has over 20 peer-reviewed publications and an h-index of 10.

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Mr. Xiaohe Tian received his BEng in 2017 from China University of Petroleum (East China) and is currently completing a Master Degree at UQ. He had almost 2-year research experience in material science and CO₂ electrochemical engineering. His current research is mainly focused on catalysts synthesized via electrodeposition for CO₂ electrochemical reaction. He is supervised by Dr. Thomas E. Rufford and Dr. Mengran Li.

Guoxiong Wang

Prof. Guoxiong (Geoff) Wang received his BEng in 1983 and MEng in 1986 and PhD in 1989 from Northeastern University of China. Before joining the University of Queensland in 1996, he was a visiting Professor at the School of Materials Science and Engineering at the University of New South Wales in 1995. He has significantly contributed to the research area of chemical metallurgy, energy and environmental technologies. He is author of a monograph entitled "Pulverized Coal Injection Technology for Blast Furnaces" and has over 100 original journal publications, 60 refereed conference papers and a patent.

Thomas E. Rufford

Dr Tom Rufford is a senior lecturer in the UQ School of Chemical Engineering and a chartered member of IChemE. Tom was awarded BE (2000) and PhD (2009) degrees in chemical engineering from UQ. He has published more than 60 journal papers and 3 book chapters, an edited book on carbon materials, and was a recipient of ARC Discovery Early Career Researcher Award (2014-16). Dr Rufford's research interests include adsorption, electrochemistry, coal seam gas, and LNG production.

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