Ternary Sn-Ti-O Electrocatalyst Boosts the Stability and Energy Efficiency of CO₂ Reduction

Guobin Wen*, Bohua Ren†, Moon G. Park, Jie Yang, Haozhen Dou, Zhen Zhang, Yap-Ping Deng, Zhengyu Bai,* Lin Yang, Jeff Gostick, Gianluigi A. Botton, Yongfeng Hu, and Zhongwei Chen*

Abstract: Simultaneously improving energy efficiency (EE) and material stability in electrochemical CO₂ conversion remains an unsolved challenge. Among a series of ternary Sn-Ti-O electrocatalysts, 3D ordered mesoporous (3DOM) Sn₀.₃Ti₀.₇O₂ achieves a trade-off between active-site exposure and structural stability, demonstrating up to 71.5% half-cell EE over 200 hours, and a 94.5% Faradaic efficiency for CO at an overpotential as low as 430 mV. DFT and X-ray absorption fine structure analyses reveal an electron density reconfiguration in the Sn-Ti-O system. A downshift of the orbital band center of Sn and a charge depletion of Ti collectively facilitate the dissociative adsorption of the desired intermediate COOH* for CO formation. It is also beneficial in maintaining a local alkaline environment to suppress H₂ and formate formation, and in stabilizing oxygen atoms to prolong durability. These findings provide a new strategy in materials design for efficient CO₂ conversion and beyond.

Introduction

The conversion of CO₂ into valuable chemicals by electrochemical CO₂ reduction reactions (CO₂RRs) offers a clean and sustainable approach towards closing the carbon loop.[1] The CO₂RR process also allows harvesting of intermittent renewable energy sources such as wind and solar.[2] Among a variety of derived chemicals, carbon monoxide (CO) and formic acid are of great interest because of their relatively lower activation potentials and their large potential market (CO for synthetic gas and formic acid for hydrogen carrier).[3] To seek efficient electrocatalytic materials, many strategies have been explored extensively, including, but not limited to, engineering morphology,[4] tuning oxidation states,[5] and synthesizing single-atom catalysts.[6] However, there are still technical challenges that hinder the commercial scale up of CO₂RR processes, such as limited energy efficiency (EE; generally lower than 60%), shorter operating lifetime (generally lower than 100 hours), and difficult separation of end products.

Tin (Sn) and partially oxidized SnO₂-based materials are one of the most promising nonprecious materials for practical CO₂RR systems,[8] as they converge CO₂ into both CO and formic acid (see Table S1 in the Supporting Information).[5a,6a] Noticeably, oxygen (O) atoms in SnO₂ play an important role in the adsorption of intermediates.[9] Nevertheless, the EE of the CO₂RR is typically limited by a low selectivity of desired product, a large overpotential (>0.8 V), and a narrow potential window.[10] Additionally, the introduction of O atoms also causes catalysts to become unstable because of the competition between metallic oxide reduction and the CO₂RR under highly cathodic conditions.[11]

Here, we propose to decorate Sn with titanium (Ti) and construct a three-dimensional ordered mesoporous (3DOM) structure to overcome existing limitations of the CO₂RR. First, added Ti atoms are revealed to preferentially absorb the oxygen atom in the COOH* intermediate, tuning the selectivity toward CO instead of formate. Second, Ti atoms are further unearthed to stabilize the lattice oxygen atoms in SnO₂, and maintain the 3DOM structure, prolonging catalyst lifetime. Third, the robust 3DOM structure results in a local environment with higher alkalinity, not only suppressing the hydrogen evolution reaction (HER), but also further hindering formate formation. Finally, the defective Ti atoms and the high local alkaline environment are experimentally proven to reduce CO₂ activation potential and expand the potential window. Therefore, our work offers a new 3DOM ternary Sn-Ti-O electrocatalyst that can efficiently convert CO₂ into CO at high cathodic energetic efficiency (EEₕ) for extended time periods, advancing Sn-based catalytic materials for scale up and practical applications of the CO₂RR.
Results and Discussion

Density-functional theory (DFT) analyses were performed to examine the atomic interactions in the Sn-Ti-O metal-oxide interface. SnO$_2$ is reported to have good activity for the CO2RR.\textsuperscript{[3b,12]} While TiO$_2$ plays an important role to maintain the structure. The samples with lower ratios of Ti ($<0.7$) cannot construct stable 3DOM structures, and a pure TiO$_2$ sample is inactive for the CO2RR (electrochemical performance session). Consequently, two models were considered in DFT simulation to consider the effect of Ti on active SnO$_2$ sites. Model I was generated (i.e. SnO$_2$ with 6 oxygen vacancies, SnO$_{2.6}$)\textsuperscript{[13]} owing to the fact that the surface tin oxide layer can be partially reduced under reaction conditions.\textsuperscript{[38]} Model II was built as Model I with three Ti atoms substituting Sn on the surface (i.e. Sn(Ti)O$_{2.6}$) to investigate the influence of Ti on active SnO$_{2.6}$ site. Model II in DFT analyses was used as a representation of the local atomic structure of active sites.\textsuperscript{[5c,13]} Two main pathways for CO and formic acid (HCOOH) production were considered for two models (see Figures S1a–c).\textsuperscript{[7a,11,12]}

From Bader charge analysis (Table 1), we found that the surface Sn atoms near Ti atoms possess a formal charge variation of $-0.547\,e$, while O atoms near Ti atoms retain their valence state ($+0.002\,e$ variation). This data infers that Ti tends to delocalize charge by releasing it to the Sn atom (Figure 1d). The projected density of states (PDOS) of the surface Sn and Ti atoms were further analyzed (Figures 1c–e). The substitution of Ti atoms causes the s, p, and d band centers of surface Sn atoms to downshift by over 2.3 eV (see Table S2).\textsuperscript{[14]} The electron density transfer from Ti to Sn has two important impacts:

(I) In favor of CO production (shortened reaction pathway). The marked downshifts of the band centers indicate that the antibonding states are filled with more electrons. The back-donation antibonding states therefore decrease (Figure 1e).\textsuperscript{[15]} Specifically, the back-donation from the valence band of Sn to the unoccupied orbital of COOH* is reduced\textsuperscript{[16]} weakening the Sn–C bond. In contrast, Ti atoms are depleted of electron density and further possess enhanced O affinity, seeking to bond with the O of COOH*.\textsuperscript{[16]} The corresponding effects—the breaking of C–O bond and weakening of Sn–C bond during adsorption process—both benefit the dissociative adsorption of the COOH* intermediate, as illustrated in Figure 1d. These results additionally reveal the change in the catalytic mechanism associated with Ti substitution. As depicted in Figure 1a, the intermediate COOH*, which is derived from CO$_3$H* and deemed as the main intermediate of CO formation, bonds on the SnO$_{2.6}$ surface (Model I) through a carbon atom (Figure 1a). Upon further transfer of H* from the electrolyte, COOH* dissociates into CO* and OH* with a reaction energy of $-2.96\,eV$ (Table 2). However, for the Sn-Ti-O system, COOH* dissociative adsorption takes place on the Sn(Ti)O$_{2.6}$ surface (Model II), leading to direct CO* formation (Figure 1b). This sequence transforms CO* formation from a two-step reaction (CO3H* $\rightarrow$ COOH* $\rightarrow$ CO*) into a one-step reaction (CO$_3$H* $\rightarrow$ CO*), which facilitates CO* production (see Figures S1d and e).

(II) Suppression of HCOOH production (higher reaction energy). For Model I (pure SnO$_{2.6}$), HCOO* is adsorbed onto the surface by forming Sn–O bond. However, for Model II (Sn(Ti)O$_{2.6}$), HCOO* tends to adsorb by forming a Ti–O bond.

\begin{table}[h]
\centering
\caption{Calculated average Bader charge (e) of surface Ti atoms and neighboring Sn and O atoms in Models I and II.}
\begin{tabular}{|c|c|c|c|}
\hline
Atom\textsuperscript{[a]} & Surface Models & Model I: SnO$_{2.6}$ & Model II: Sn(Ti)O$_{2.6}$ & Variation (\Delta e) \\
\hline
O (av) & $-1.063$ & $-1.061$ & $+0.002$ \\
Sn (av) & $+1.390$ & $+0.843$ & $-0.547$ \\
Ti (av) & $-1.745$ & $-1.745$ & \\
\hline
\end{tabular}
\textsuperscript{[a]} O (av) and Sn (av) entries indicate the average (av) charges of three O atoms and three Sn atoms, respectively, located at the nearest neighboring sites of Ti.
\end{table}

\begin{table}[h]
\centering
\caption{Calculated reaction energies ($\Delta E$) of Model I and II.}
\begin{tabular}{|c|c|c|}
\hline
Reactions & Surface Models & Model I: SnO$_{2.6}$ & Model II: Sn(Ti)O$_{2.6}$ \\
\hline
COOH* $\rightarrow$ OH* $+$ H* $+$ e$^-$ & $-2.96\,eV$ & $-3.33\,eV$ \textsuperscript{(i)} \\
$\rightarrow$ CO* $+$ H$_2$O* $+$ OH* & \\
HCOO* $\rightarrow$ OH* $+$ H* $+$ e$^-$ & $-3.39\,eV$ & $-2.49\,eV$ \\
$\rightarrow$ HCOOH* $+$ OH* & \\
\hline
\end{tabular}
\textsuperscript{(i)} the reaction energy for CO* formation step is calculated by using $E$(CO$^0$ $+$ 2OH$^0$)$-E$(COH$^0$ $+$ H$^+$) due to dissociative adsorption of COOH$^*$ for Model II (see Figure S1).
\end{table}
bond instead (Figure 1f). The Ti atoms introduced in the pure SnO\textsubscript{2−x} system interacts with neighboring Sn atoms. As shown in Figure 1f, Sn atoms deplete Ti atoms of electron density. Consequently, Ti atoms further possess enhanced O affinity, which indicates that the Ti–O bond is stronger than Sn–O bond. This finding is also supported by the stronger adsorption of HCOO\textsuperscript{*} on Model II. As indicated by the definition of adsorption energy (\(E_{\text{ads}}\)) in the Supporting Information, a more negative value of \(E_{\text{ads}}\) means stronger adsorption. As shown is Table S3, \(E_{\text{ads}}\) of HCOO\textsuperscript{*} on Model II is \(-3.11\) eV, while \(E_{\text{ads}}\) is \(-2.20\) eV on Model I. The much higher adsorption strength (more negative) makes the HCOO\textsuperscript{*} intermediate overly stabilized, making it more difficult to break the Ti–O bond and produce HCOOH\textsuperscript{*}, as shown in Figure S1b. In addition, the higher adsorption energy of HCOOH\textsuperscript{*} on Model II, as shown in Table S3, leads to unfavorable desorption. The above reasons justify the higher reaction energy for HCOOH\textsuperscript{*} production in Model II than Model I, causing a suppression of HCOOH\textsuperscript{*} in Model II. Accordingly (see Table S4), the variation in reaction energies indicate that CO formation is more spontaneous and formation of HCOOH\textsuperscript{*} is suppressed for Model II.

As disclosed by DFT calculations, with appropriate construction of ternary Sn-Ti-O catalysts, Ti atoms tend to delocalize charge by releasing it to the Sn atoms. This delocalization may explain why selectivity is shifted towards CO rather than formate.

In light of Sn–Ti interactions and previously reported superiorities of mesoporous structure\textsuperscript{[17]} we sought to produce 3DOM ternary Sn-Ti-O compounds, which were prepared according to our previous work\textsuperscript{[18]} A series of ternary Sn-Ti-O catalysts with varying surface ratios of Sn-Ti were synthesized and characterized: Sn\textsubscript{0.1}Ti\textsubscript{0.9}O\textsubscript{2}, Sn\textsubscript{0.2}Ti\textsubscript{0.8}O\textsubscript{2}, Sn\textsubscript{0.3}Ti\textsubscript{0.7}O\textsubscript{2}, Sn\textsubscript{0.4}Ti\textsubscript{0.6}O\textsubscript{2}, Sn\textsubscript{0.6}Ti\textsubscript{0.4}O\textsubscript{2}, Sn\textsubscript{0.8}Ti\textsubscript{0.2}O\textsubscript{2} (see Table S5). Among these, the Sn\textsubscript{0.3}Ti\textsubscript{0.7}O\textsubscript{2} catalyst had the best selectivity for CO formation as discussed in the later electrochemical performance section.

The produced ternary Sn-Ti-O materials were characterized using scanning electron microscopy (SEM) and observed an evident honeycomb porous structure, as shown in Figure 2a and Figure S2. The structure exhibited consistent pores with a diameter of approximately 100 nm (Figure 2b), providing strong structural support and high surface area with many available sites for catalytic activity. Interestingly, only for certain Sn-Ti-O ratios (Sn\textsubscript{0.2}Ti\textsubscript{0.8}O\textsubscript{2} and Sn\textsubscript{0.3}Ti\textsubscript{0.7}O\textsubscript{2}; see Figure S3 and S4), there were 5 nm nanoparticles attached on the 3DOM framework (Scheme 1 and Figure 2b, inset).

Figure 2c depicts a compositional line scan on the edge of the porous structure of the 3DOM Sn\textsubscript{0.3}Ti\textsubscript{0.7}O\textsubscript{2} material, showing the composition of Sn, Ti, and O elements. As further shown in Figure 2d and Figure S3, the chemical compositional maps with electron energy loss spectroscopy (EELS) were obtained over the region shown within the green box. The results showed a 3DOM framework with adherent nanoparticles composed of SnO\textsubscript{2} with dispersed amorphous/crystallographic (anatase) TiO\textsubscript{2} in the Sn\textsubscript{0.3}Ti\textsubscript{0.7}O\textsubscript{2} material (Scheme 1). High-resolution TEM (HRTEM) was performed on this 3DOM structure, which showed a d-spacing corresponding to the (110) and (101) planes of SnO\textsubscript{2} and the (211) and (105) planes of anatase TiO\textsubscript{2}, and the amorphous layer (Figure 2e). The same conclusions were derived from the compositional line scan, chemical compositional maps, and HRTEM of Sn\textsubscript{0.3}Ti\textsubscript{0.7}O\textsubscript{2} material, which are provided in Figure S4.

Hierarchically ordered and interconnected mesoporous structure of synthesized Sn-Ti-O materials were found to feature a type IV \(N_2\) adsorption-desorption isotherm\textsuperscript{[19]} as shown in Figure S5. Particularly, the Sn\textsubscript{0.3}Ti\textsubscript{0.7}O\textsubscript{2} material showed a Brunauer-Emmet-Teller (BET) specific surface area of 39.9 m\(^2\) g\(^{-1}\) and a less broad pore size distribution. This special structure appears to achieve an ideal balance between
exposure of active sites (more Sn-Ti-O interface) and appropriate electron density shift to enable a Sn-Ti-O ternary synergetic effect and display optimum CO2RR performance as depicted by electrochemical tests, to be discussed later. The formation of such special structures, with nanoparticles attached to the surface of 3DOM framework can be ascribed to the selective surface migration, phase separation, and oxidation of the metals during calcination.[19]

Given the nature of sample fabrication (co-precipitation and calcination at 600 °C), it is possible to thermodynamically observe formation of Sn-Ti intermetallic as well as mixed-oxide phases as indicated in the phase diagrams (see Figures S6a,b). The X-ray diffraction (XRD) technique has deep penetration and provides a glimpse of the material compositions. As depicted from XRD patterns (Figure 2f; see Figure S7a), the special Sn0.3Ti0.7O2 composition displayed a major SnO2 phase. However, as shown in Figure 2c–e (line scan from EELS spectra; elemental mapping; HRTEM images), there were still coexisting amorphous and anatase TiO2 phases, presumably near the surface of the 3DOM framework. Given TiO2 is mainly amorphous and the amount of anatase TiO2 is limited, the peaks of SnO2 dominated and TiO2 peaks could not be observed in the XRD patterns.

For the higher Sn-Ti ratios (Sn0.4Ti0.6O2, Sn0.5Ti0.5O2, Sn0.6Ti0.4O2), XRD patterns still clearly revealed only peaks of SnO2, and the Ti atoms likely existed as poorly crystalline oxides. Although the pure SnO2 sample formed an extensive 3DOM structure, with low additions of TiO2, the SnO2 phase tended to congregate and formed nanoparticles with the influence of Ti additions, thereby interrupting the framework, as shown in Figure S8. From TEM images (see Figure S9), the 3DOM formation became more stable for Sn0.2Ti0.8O2, suggesting higher additions of TiO2 eventually stabilize the structure.

In contrast, for a lower Sn-Ti ratio (Sn0.1Ti0.9O2, Sn0.2Ti0.8O2, Sn0.3Ti0.7O2), there was evidence of peak broadening and peak shoulder/separation at around 27°, 35°, and 51° in the XRD patterns (see Figure S7a), presumed to correspond to the spinodal decomposition region (see Figure S6a), displaying a more defined coexistence of SnO2 and anatase TiO2 phases. In this case, formation of TiO2-rich regions caused shifting and transition of SnO2 peaks towards TiO2 anatase. At 100 mol% TiO2 composition, the phase diagram predicts a rutile phase.[20] Interestingly, our 3DOM structure appeared as anatase, which has higher catalytic activity than the rutile phase.[21] Considering the differences between nanomaterial and bulk material solidification, the deviation from the phase diagram is understandable. The 3DOM nanostructure presents itself with a larger solubility range and formation of anatase rather than rutile because of: 1) the extra energy applied during the sonication procedure, 2) possibility of liquid and solid phase coexistence in small dimensions,[22] and 3) more Ti accommodation because of atomic segregation towards the surface, which avoids nucleation of another phase.[23] The special Sn-Ti ratio (Sn0.3Ti0.7O2) is most likely the crucial turning point for spinodal decomposition for the nanobinary materials (see Figure S6c), Sn0.3Ti0.7O2 not only avoided complete spinodal decomposition, presenting mainly a SnO2 phase with a minor amorphous/anatase TiO2 phase, but also maintained a stable 3DOM structure.

As we previously disclosed,[12a] the Sn-based catalysts need to undergo accelerated degradation and activation under −1.13 V vs. RHE before performing the CO2RR.[19] The emergence of Sn peaks was found for the electrodes with Sn-Ti ratios higher than 3:7, after the in situ activation step (see Figure S7). After the activation step, notably, the SnO2 peaks were still conserved for Sn0.3Ti0.7O2 electrodes, while there were no remaining strong SnO2 peaks for the 3DOM SnO2 electrode after activation. Further, for lower Sn-Ti ratios (Sn0.8Ti0.2O2 and Sn0.7Ti0.3O2), the oxide-to-metal phase exchange (i.e., reduction of SnO2 to Sn) was not noticeable from XRD analysis. This resistance to phase change is understood to be due to the oxygen atoms being much more stable in the Sn-Ti-O ternary structure during the CO2RR.

To explore the complex interactions and the electronic structure between Sn, Ti, and O atoms, the calculated charge density reconfiguration is disclosed in Figure 3a and shows that the charge density is accumulated around O and Sn atoms, while depleted around Ti atoms.[18,23] To further verify the electron density configuration of Ti in the catalysts, X-ray absorption near-edge spectroscopy (XANES) at the Ti K-edge was performed to illustrate the coordination environments of Ti in different cases. Three characteristic features are denoted A1, A2, and A3 in the pre-edge structure of the Ti K-edge spectra of compounds with high structural symmetry, such as six-coordinated anatase (Figure 3b).[24] For all Sn-Ti-O materials, A1 and A3 signals were weak; only a pronounced A2 peak was perceived instead, indicating the existence of less symmetric Ti atoms predominately on the surface of the oxides.[25] The low-coordination nature of Ti is also supported by the amorphous structure of TiO2 as depicted by XRD patterns (i.e., no clear discrete diffraction peaks associated with anatase TiO2; see Figure S7), HRTEM (Figure 2c, and
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Our FEM calculation results further validate the ability of our mesoporous structure to increase CO selectivity, by not only suppressing the HER, but also hindering formate formation. The bicarbonate electrolyte has low buffer capacity with limited migration rates of ionic species. It results in two consequences: 1) limited hydroxide ion migration rates and increased local alkalinity restricts the availability of protons in the mesopores, which inhibits the HER activity; 2) limited formate ion migration rates and increased formate ions concentration in the mesopores (see Figure S15) further hinder formate formation. Additionally, a highly alkaline region is also beneficial for the catalytic activation of CO₂ in the electrolyte, as proven by XPS spectra (see Figure S18). To maintain a constant ionic concentration in the electrolyte during prolonged testing, the electrolyte was replaced with fresh solution every 20 hours and the recorded time step was set to 30 minutes. To demonstrate structural robustness, we altered the potential during the stability test. As the Snₓ₋₀.₃Tiₓ₋₀.₇O₂– electrode had good stability of over 200 hours of continuous electrolysis (orange curve in Figure 4f), we were able to maintain CO₂ availability, which is an impressive feature for CO₂RR.

In summary, 3DOM ternary Sn-Ti-O catalysts were successfully produced, representing a simple but highly effective artificial material for CO₂RR. DFT calculations combined with different physical and chemical characterizations revealed the nature of the electron density reconfiguration among Sn, Ti, and O atoms. A balance between exposure of active sites and degree of electron density shift was imperative for achieving a highly efficient 3DOM catalyst. In particular, it was inferred that the crucial electron-density transfer from Ti to Sn enabled the dissociative adsorption of COOH, directly producing CO with a cathodic energy efficiency over 71.5%. The existence of Ti not only effectively creates an electron bank which contributes to activation of catalytic reactions, but it also plays an important role in strengthening the 3DOM structure to maintain a high EE for over 200 hours within a wide potential window. Insights gained through these quantitative
analyses of electron density configuration can be further exploited as promising design principles for high-performance catalysts, making the electrochemical process more sustainable for practical applications.

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Conflict of interest

The authors declare no conflict of interest.

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Ternary Sn-Ti-O Electrocatalyst Boosts the Stability and Energy Efficiency of CO₂ Reduction

Trade off: With a trade-off between active-site exposure and structural stability, a 3D ordered mesoporous (3DOM) structured Sn-Ti-O material achieves cathodic energy conversion efficiency (EEca) as high as 71.5% over 200 hours for electrochemical conversion of CO₂ into CO. It benefits from an electron density reconfiguration at the Sn-Ti-O interface and a local alkaline environment to improve CO selectivity and stabilize lattice oxygen atoms.