1nm Tin Oxide Cluster for the Electrochemical Conversion of Carbon Dioxide to Formate at Low Overpotential

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Due to its cost-effectiveness and high product selectivity, tin oxide has been regarded as a promising catalyst for the electrochemical conversion of CO2 to formate. However, formate production is hindered by the high overpotential; there is a need to reduce the overpotential to enhance energy efficiency and lower electricity cost for the implementation of carbon utilization technology. Here, we report a facile synthesis method for 1 nm-sized SnO2 cluster catalysts, which can be used for CO2-to-formate conversion. SnO2 clusters were prepared through impregnation of porous carbon with a tin precursor solution. The SnO2 clusters showed a low overpotential, generating a current density of 10 mA cm\(^{-2}\) at a potential of -0.34 V vs. RHE in 1 M KOH. They also achieved high Faradaic efficiencies of 90.5% and 81.5% at 200 and 300 mA cm\(^{-2}\), respectively. Their electrocatalytic performance was strongly dependent on the annealing conditions, which affected the particle size, electrochemical active surface area, and metal oxidation state. This paper presents a versatile method for synthesizing metal oxide cluster catalysts, apart from providing insights into the catalytic activity for the electrochemical conversion of CO2 to formate.

1. Introduction

Carbon dioxide (CO2) is one of the primary greenhouse gases that have significantly contributed to climate change; it is generated by human activities, especially the combustion of fossil fuels [1–3]. Electrochemical conversion of CO2 is a promising method for mitigating the problem of anthropogenic carbon emissions. CO2 can be converted into valuable chemicals, such as carbon monoxide (CO), formic acid, methane, and ethylene [4–8]. Formate can be produced using only two electrons, and it is used for various purposes in different industrial sectors. These include the production of pharmaceuticals, crop protection agents, rubber, silage, animal feed, and textile dyeing [9–13]. In particular, formic acid can be used as a hydrogen carrier because of its high hydrogen capacity (53 g of H\(_2\)/L), and it is advantageous for hydrogen storage and transportation since it is a liquid at room temperature [13–15].

Electrocatalysts play a crucial role in determining the overpotential and selectivity in the electrochemical reduction of CO2. Among various electrocatalysts, tin-based catalysts have been extensively studied because of their high activity, low cost, nontoxicity, and earth abundance [16–18]. Specifically, tin oxide catalysts have been reported to play a pivotal role in facilitating the CO\(_2\) reduction reaction (CO\(_2\)RR). For example, Chen and Kanan [19] developed an Sn/SnO\(_2\) catalyst that exhibited threefold higher activity for formate and fourfold higher activity for CO than metallic Sn catalysts. On the basis of the Tafel slope analysis, the high activity was attributed to the stabilization of CO\(_2\) intermediates on the tin oxide surface. Hydroxyl groups on the surface of SnO\(_2\) catalysts have been reported to promote formate production through a carbonate pathway [12, 20–22]. This reaction pathway involves the reaction of a CO\(_2\) molecule with a surface hydroxyl group (OH\(^*\)) to form a carbonate intermediate (HCO\(_3\)\(^*\)), which is then converted into COOH\(^*\) or OCHO\(^*\) intermediates. These intermediates are further converted into formate or formic acid [23].

Electrocatalysts derived from metal-organic frameworks (MOFs) have been actively researched in the field of CO\(_2\)RR because of their high porosity, tunable pore size, efficient mass transport, and CO\(_2\) adsorption properties [24–28]. In
particular, porous nitrogen-doped carbon derived from MOFs is widely used as an electrocatalyst in the CO$_2$RR since it promotes the dispersion of supplementary nanocatalysts used in the reaction; the dispersion results from chemical interactions between the nanocatalysts and the N-doped surface [27, 29, 30]. This synthetic strategy can also be used to stabilize metal oxide nanoclusters. With a decrease in the particle size of metal oxide clusters, the surface-to-volume ratio increases, and the surface becomes more active [31–33]. Thus, metal oxide clusters with a small particle size can provide a highly active catalyst surface for formate production through the CO$_2$RR.

Here, we present a method for the facile preparation of SnO$_2$ clusters supported on ZIF-8-derived porous carbon (ZC; the combination of SnO$_2$ clusters and ZC is hereafter referred to as SnO$_2$/ZC). Empty mesopores were impregnated with SnO$_2$ clusters by simply immersing the porous carbon in a tin precursor solution and vacuum drying it at room temperature. We also investigated the effect of heat treatment on SnO$_2$ clusters by annealing SnO$_2$ clusters at different temperatures and in different atmospheres. The as-prepared SnO$_2$ cluster catalyst exhibited the best performance, with a Faradaic efficiency (FE) of 90.5% for formate production at a potential of −0.67 V vs. RHE and a current density of 200 mA cm$^{-2}$ in 1 M KOH electrolyte. It also showed a superior onset potential of −0.34 V vs. RHE to reach 10 mA cm$^{-2}$. Transmission electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS) analyses showed that the SnO$_2$ clusters were well dispersed on the ZC surface and had a hydroxyl-rich nature. Heat treatment affected the particle size, electrophysically active surface area (ECSA), and metal oxidation state, adversely affecting the CO$_2$RR activity of SnO$_2$/ZC.

2. Experimental Section

2.1. Chemicals and Materials. Deionized (DI) water (18.2 MΩ·cm$^{-1}$, SimPure 330D), Zn(NO$_3$)$_2$·6H$_2$O (98.0%, Daejung), 2-methylimidazole (99%, Thermo Fisher Scientific Inc.), methanol (99.5%, Daejung), isopropyl alcohol (99.5%, Daejung), 5% Nafion solution (Alfa Aesar), SnCl$_2$ (98%, Daejung), acetone (99.5%, Daejung), Ar gas (99.999%, Dong-A Specialty Gases), Ar/H$_2$ (8%) gas (Dong-A Specialty Gases), CO$_2$ gas (99.999%, Dong-A Specialty Gases), KOH (93%, Daejung), KHCO$_3$ (99.5%, Daejung), a gas diffusion electrode (GDE; Sigracet 39BB), and a Nafion 117 membrane (DuPont) were used in this study.

2.2. ZIF-8 Preparation. To synthesize ZIF-8, 1.28 g of Zn(NO$_3$)$_2$·6H$_2$O and 3.28 g of 2-methylimidazole were mixed with 100 mL of methanol. The mixture was stirred at 200 rpm and 60°C for 1 h, followed by centrifugation at 8000 rpm for 5 min. The precipitate obtained was washed thrice with methanol, centrifuged at 8000 rpm for 30 min, and dried in an oven overnight at 60°C.

2.3. ZC Preparation. The dried ZIF-8 was carbonized for 30 min at 1000°C in an Ar atmosphere with a heating rate of 5°C/min, and the carbonized ZIF-8 was treated with 0.5 M H$_2$SO$_4$ at 80°C for 1 h. After 1 h, the treated ZIF-8 was washed with deionized (DI) water to neutralize its pH and remove any residual impurities.

2.4. Sn/ZC Preparation. An amount of 100 μL of a 0.8424 M solution of SnCl$_2$ in acetone was added to 20 mg of the acid-treated ZC, and the acid-treated ZC sample was sonicated for 1 h and dried in a vacuum oven at room temperature for 2 h. This three-step process was performed twice. The heat-treated catalyst was placed in a tube furnace in an Ar/H$_2$ (8%) atmosphere, and it was heated to temperatures of 100°C, 200°C, and 300°C at a heating rate of 5°C/min.

2.5. GDE Preparation. Sn/ZC ink was prepared by mixing 10 mg of Sn/ZC, 200 μL of the 5% Nafion solution, and 10 mL of isopropyl alcohol. The mixture was then sonicated for 30 min. The sonicated ink was sprayed onto a 1 cm × 1 cm piece of Sigracet 39BB. The total catalyst loading was 3.0 mg cm$^{-2}$. The ink-sprayed electrode was then heat-treated in an oven at 60°C for 30 min.

2.6. Characterization. The crystallinity of the catalyst structure was determined using X-ray diffraction (XRD; Ultima IV, Rigaku) with Cu Kα radiation (λ = 0.15406 nm). The morphology of the catalyst was characterized using TEM (JEM-2100F, JEOL, Ltd.) at an acceleration voltage of 200 kV. The size distribution was obtained by analyzing high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images with the Image software. The chemical state and atomic concentration of the samples were determined using XPS (ESCALAB 250, Thermo Scientific). The binding energy of the C 1s peak in the XPS spectrum was calibrated to 284.5 eV.

2.7. Electrochemical Measurements. The electrochemical performance of the synthesized catalyst was analyzed using a three-electrode system. The Nafion 117 membrane was inserted between the working and counter electrodes. Nickel foam and a Hg/HgO electrode were used as the counter and reference electrodes, respectively. Experiments were conducted in 1 M KOH (pH 14) electrolyte using a potentiostat (Ivium), and the potentials obtained were converted to the RHE scale (E$_{\text{RHE}}$ = E$_{\text{Hg/HgO}}$ + 0.098 V + 0.0591 V × pH). The H$_2$ and CO concentrations were measured using gas chromatography (GC; YL Chromass) every 15 min in 30 min of electrolysis. And the formate concentration was measured using nuclear magnetic resonance (NMR; AVANCE III 400 MHz, Bruker). For $^1$H NMR measurement, 700 μL of the catholyte sample was mixed with 35 μL of an internal standard solution (D$_2$O + 10 mM of DMSO + 50 mM of phenol).

2.8. In Situ Raman Measurement of As-Prepared Catalyst. In situ Raman measurements were conducted using a Raman electrochemical flow cell (Redoxme) with a sapphire window. The counter and reference electrodes were Pt wire and Ag/AgCl electrodes, respectively. For the working electrode, a 1 mm × 1 mm catalyst deposited on carbon paper was directly used using Ta wire as the current collector. CO$_2$-saturated 0.5 M KHCO$_3$ electrolyte was circulated to fill the cell by a peristaltic pump. The applied potential was
controlled with the Ivium potentiostat. The potentials against reference were converted to RHE using this equation: ERHE = EAg/AgCl + 0.1976 + (0.0591 × pH).

3. Results and Discussion

The SnO2/ZC cluster catalysts were synthesized using a facile impregnation method. Due to the molecular adsorption capability inherent in ZIF-8-derived carbon, it effectively retains small molecules within its porous structure [34, 35]. Carbon powder was added to an SnCl2-containing acetone solution, and the solution was sonicated and then dried in a vacuum oven at room temperature. As-prepared SnO2/ZC was prepared without annealing, whereas heat-treated SnO2/ZC catalysts were placed in a tube furnace and subjected to different temperatures under different atmospheres (Ar 100°C, Ar/H2 100°C, and Ar/H2 300°C).

XRD analysis was conducted to investigate the crystal structure of the catalyst samples prepared at different annealing temperatures and without heat treatment. The XRD patterns of all the samples showed a tetragonal SnO2 phase that matched well with the reference (JCPDS card no. 41-1445). The diffraction patterns sharpened at a high temperature of 300°C because the crystallite size increased. Sharp peaks that were observed for some samples (Ar 100°C) were assigned to a small amount of the SnCl2 impurity phase (SnCl2 had been added to the precursor solution). TEM analysis was performed to investigate the nanostructural properties and elemental distribution. High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images (Figures 1(b) and 1(c)) of the as-prepared SnO2/ZC catalyst showed that ~1 nm SnO2 clusters were well deposited on the porous carbon support (Figure S3). The porous nature of ZIF-8-derived carbon facilitated the absorption of the SnCl2 precursor solution via the capillary effect. Scanning transmission electron microscopy–energy-dispersive X-ray spectroscopy mapping analysis (Figure S1) showed that the Sn, O, and C elements were uniformly distributed on the porous particle. The SnO2 particles grew when annealing was performed at high temperatures (Figure S2). As shown in Figure 1(d), the particle size increased from approximately 1.02 to 2.61 nm when the SnO2/ZC catalyst was annealed at 300°C, which was in agreement with the XRD result (Figure 1(a)).

According to a previous study [36], the CO2 reduction reaction mechanism on SnO2 involves a bicarbonate-intermediate pathway. This pathway initiates the interaction between adsorbed OH and CO2, resulting in the formation of an adsorbed bicarbonate (CO3H•) species. The CO3H• intermediate undergoes subsequent reactions with H+ and electron transfer, leading to the formation of *HCOO and *OH. The release of HCOOH follows as HCOO• reacts with another H+ and acquires an additional electron. Another potential mechanism for producing HCOOH involves the insertion of CO2 into the metal-H bond, leading to the formation of the *HCOO intermediate, from which HCOOH is then derived through *HCOO reduction. The surface hydride plays a role in reducing CO2 to form the *HCOO intermediate. Another reaction pathway, characterized by an O-bound intermediate, commences with the initial electron transfer to CO2, resulting in the formation of a CO2• radical intermediate weakly adsorbed onto the surface. Formic acid is generated through the transfer of protons and electrons facilitated by reactions between the CO2• radical and proton donors such as water, bicarbonate, and hydroxide ions. In the pathway involving a C-bound intermediate, the CO2• radical is initially generated and subsequently binds to the catalyst surface through the C atom. Following this, the CO2• radical reacts with H+ to create an adsorbed *COOH species. Then, HCOO*/HCOOH can be generated from *COOH.

XPS analysis was conducted to acquire a comprehensive understanding of the metal valency and surface properties of the SnO2/ZC catalysts. Figure 1(e) shows the XPS core-level spectra of the Sn 3d region for each catalyst. For the as-prepared sample, the XPS peaks at around 496.0 and 487.5 eV can be assigned to the Sn 3d3/2 and Sn 3d5/2 orbitals of SnO2, respectively [37], indicating Sn 4+ state. The binding energy of the Sn 3d3/2 peak slightly shifted toward lower energy values of 487.4 and 487.2 eV after annealing at 100°C and 300°C under an Ar/H2 atmosphere, respectively. This resulted from some Sn atoms being reduced to the 2+ oxidation state under the reducing atmosphere. The binding energy of Sn2+ oxide has been reported to be 486.4 eV [38]. Figure 1(f) shows the XPS O 1s spectra of the prepared SnO2/ZC catalysts. The peaks at 530.8 and 532.4 eV are assigned to the Sn–O and Sn–OH species present in SnO2, respectively [39]. It was observed that heat treatment decreased the intensity of the Sn–OH peak and relatively increased the intensity of the Sn–O peak. In the absence of heat treatment (e.g., the as-prepared catalyst), hydroxyl species was the dominant oxygen species. This trend can be understood by considering the dehydration and particle growth that occur during annealing. Thermal energy can promote adsorbate evaporation, resulting in the surface hydroxyl species being removed. Furthermore, annealing can promote particle growth and cause the removal of defective surface sites, thereby reducing the adsorption ability of the catalyst.

Chronopotentiometric electrolysis was conducted at various current densities in the range of 10–200 mA cm−2 in 1 M KOH electrolyte to investigate the CO2RR performance of the prepared SnO2/ZC catalysts. A flow cell equipped with a catalyst-coated GDE was used for the electrochemical test. Figure 2(a) shows total current density vs. potential curves for the SnO2/ZC catalysts prepared without annealing (as-prepared) and annealed under different temperatures and atmospheres. The as-prepared SnO2/ZC catalyst not only exhibited the lowest overpotential of ~0.67 V vs. RHE at 200 mA cm−2 but also showed a superior onset potential of ~0.34 V vs. RHE to reach 10 mA cm−2. Since the equilibrium potential of formate is ~0.03 V vs. RHE [40], the overpotential of the as-prepared SnO2/ZC was measured as 310 mV at 10 mA cm−2. The thermally treated SnO2/ZC catalysts and commercial SnO2 nanoparticles (NPs) showed much higher overpotentials. In general, the overpotential of the catalysts increased with the annealing temperature and in the presence of a reducing atmosphere.
Figure 1: (a) XRD patterns of the SnO₂/ZC cluster prepared without annealing (as-prepared) and those annealed under different temperatures and atmospheres (Ar 100 °C, Ar/H₂ 100 °C, and Ar/H₂ 300 °C). The referenced XRD patterns of SnO₂ (JCPDS #41-1445) are displayed at the bottom. (b) HAADF-STEM and (c) high-resolution TEM images of the as-prepared SnO₂/ZC catalyst. Visualization of SnO₂ nanoclusters within the delineated yellow square, exhibiting a size of approximately 1 nm. (d) Particle size distribution of SnO₂/ZC catalysts prepared under different annealing conditions. (e) Sn 3d and (f) O 1s XPS spectra of the as-prepared and the heat-treated SnO₂/ZC catalysts.
Figure 2: (a) Plots of the total current density vs. potential for the SnO$_2$/ZC catalysts prepared without annealing (as-prepared) and annealed under different temperatures and atmospheres (Ar 100°C, Ar/H$_2$ 100°C, and Ar/H$_2$ 300°C). Electrochemical data of commercial SnO$_2$ NPs are also plotted for comparison. HCOO$^-$, H$_2$, and CO FEs of (b) the as-prepared sample and the annealed samples prepared under different conditions, namely, (c) Ar 100°C, (d) Ar/H$_2$ 100°C, and (e) Ar/H$_2$ 300°C. (f) Plot of the partial current density used for formate production as a function of the potential for various SnO$_2$/ZC catalysts.
Figure 3: (a) Electrochemical double-layer capacitance of the as-prepared and heat-treated SnO₂/ZC catalysts. ECSA-normalized partial current densities for (b) HCOO⁻ and (c) H₂ production on the prepared SnO₂/ZC catalysts are also shown. (d) Total current density vs. potential curves and (e, f) FEs of the as-prepared SnO₂/ZC catalyst with 5 and 10 wt% polytetrafluoroethylene (PTFE) content.
The gas and liquid products were quantified using online GC and H NMR analyses to evaluate the FEs of each catalyst for formate production. As shown in Figure 2(b), the as-prepared SnO$_2$/ZC showed a high FE value of 69.6% at -0.34 V vs. RHE (at 10 mA cm$^{-2}$). The FE value increased with the overpotential, reaching 90.5% at -0.67 V vs. RHE (at 200 mA cm$^{-2}$). In comparison, the heat-treated catalyst annealed at 100°C under an Ar atmosphere exhibited slightly lower FEs of 63.5% and 85.8% at similar potential values of -0.35 and -0.67 V vs. RHE, respectively (Figure 2(c)). Other heat-treated samples (Ar/H$_2$ 100°C and Ar/H$_2$ 300°C) also exhibited considerably lower FE values of 66.8% and 34.8% at -0.66 and -0.68 V vs. RHE (Figures 2(d) and 2(e)). Simultaneously, H$_2$ evolution from a competing reaction increased. These results indicate that heat treatment caused the SnO$_2$/ZC catalyst to become more selective toward hydrogen evolution. We plotted the partial current density for formate production as a function of the potential (Figure 2(f)). To determine the optimal annealing temperature condition, experiments were conducted, including trials at 200°C. However, the as-prepared sample displayed significantly superior performance compared to these conditions (Figure S4). The result confirmed that the as-prepared SnO$_2$/ZC catalyst showed outstanding performance for the electrochemical conversion of CO$_2$ to formate at a low overpotential and high current densities.

The electrochemical double-layer capacitance method was used to measure the ECSA, and cyclic voltammetry scans were performed at different scan rates (Figure S5). Figure 3(a) shows the double-layer capacitance ($C_{dl}$) values of the as-prepared and heat-treated SnO$_2$/ZC catalysts. The as-prepared catalyst had the highest $C_{dl}$ value, and the annealed samples showed a lower $C_{dl}$ value at higher annealing temperatures. This trend is consistent with the particle size distribution result (Figure 1(d)), which indicated that the SnO$_2$ particle size increased with the annealing temperature, leading to a decrease in the ECSA. A lower ECSA necessitates a high overpotential to generate the same current density.

The ECSA-normalized partial current densities for HCOO$^-$ and H$_2$ production were plotted as a function of
the potential to evaluate the intrinsic activity of the catalysts for the CO₂RR (Figures 3(b) and 3(c)). The SnO₂/ZC catalysts treated under a hydrogen atmosphere showed poor intrinsic activities toward formate production, whereas the as-prepared catalyst exhibited an approximately 68-fold higher intrinsic activity at −0.67 V vs. RHE. The SnO₂/ZC sample annealed at 100°C under an Ar atmosphere also showed a similar high activity. Furthermore, the intrinsic hydrogen evolution reaction activity was the highest for the sample treated at 300°C under an Ar atmosphere. These results indicate that reductive treatment severely degrades the active sites of catalysts. In other words, the oxidation state of tin oxide is one of the key factors that determine the CO₂RR activity in SnO₂/ZC catalysts. This inference is in good agreement with the findings of previous reports [41–44].

To control the hydrophobicity and mass transfer ability of the catalyst-coated GDE, we added PTFE to the catalyst dispersion and spray-coated the mixture onto the GDE. As shown in Figure 3(d), without PTFE (PTFE: 0 wt%), the overpotential increased too much at 300 mA cm⁻² and the H₂ FE also increased significantly (Figure S6). It was assumed that flooding behavior inhibited CO₂ transport and led to the required high overpotential [45]. When PTFE was added to the catalyst, the overpotential was significantly improved over the entire current range and hydrogen evolution was suppressed (Figures 3(d)–3(f)). However, CO evolution tended to increase with the PTFE content. CO FEs were evaluated to be 7.9%, 7.4%, and 14.7% for 0, 5, and 10 wt% PTFE content, respectively, at potentials around -0.65 V vs. RHE. At the optimum PTFE content of 5 wt%, we achieved a low overpotential of -300 mV to drive 10 mA cm⁻² and a high FE of 81.5% at 300 mA cm⁻² at -0.33 V vs. RHE. The addition of excessive PTFE to the catalyst layer could repel the electrolyte and decrease the ECSA [46].

With these optimal conditions, long-term electrolysis was conducted at -100 mA cm⁻² (Figure 4(a)). The potential value was found to be stably maintained within 47 mV degradation. The FEs for H₂ and CO production were also suppressed below 2.7% and 11.9%, respectively, during the 10 h chronopotentiometry. The FE for formate production was measured after long-term electrolysis, and it was 81.2%, indicating stable CO₂RR performance. Compared with previously reported tin oxide catalysts [41, 44, 47–54], the as-prepared SnO₂/ZC catalyst showed noticeable performance in terms of the onset potential and overpotential (Figure 4(b)), which indicated its superior CO₂ activation ability. In situ Raman spectroscopy was also used to investigate the stability during the CO₂RR (Figure S7). At OCP, a featured peak appeared at 452 cm⁻¹, which can be assigned to the vibration mode of Sn–O [55]. After applying negative potentials, there is no obvious change in the Sn–O peak, suggesting its stability during CO₂RR. However, after an extended period of electrolysis, we observed minor flooding on the backside of the cathode, accompanied by a slight decrease in potential, indicating potential cathode degradation. These findings suggest the necessity for further investigation.

4. Conclusion
We successfully synthesized 1 nm-sized SnO₂ clusters on a ZIF-8-derived porous carbon support by using a facile impregnation method. The SnO₂/ZC catalyst was heat-treated at various temperatures (100–300°C) under different atmospheres (Ar and Ar/H₂) to investigate the effect of heat treatment on the CO₂RR activity. The as-prepared SnO₂/ZC catalyst showed much higher FEs and lower overpotentials than heat-treated SnO₂/ZC catalysts for formate production owing to its larger electrochemical surface area and higher oxidation state. The SnO₂ cluster showed a low overpotential, generating a current density of 10 mA cm⁻² at a potential of -0.34 V vs. RHE in 1 M KOH electrolyte. When PTFE, a hydrophobic polymer, was added to the catalyst, high Faradaic efficiencies of 90.5% and 81.46% were achieved at 200 and 300 mA cm⁻²; moreover, hydrogen evolution was reduced, and flooding behavior was inhibited. This paper presents a versatile synthesis method for metal oxide cluster catalysts and provides insights into the catalytic activity for the electrochemical conversion of CO₂ to formate.

Data Availability
No underlying data was collected or produced in this study.

Conflicts of Interest
There are no conflicts of interest to declare.

Authors’ Contributions
C.W.L., H.R.K., and K.H.L. proposed the project, designed the experiments, and wrote the manuscript; H.R.K. and K.H.L. performed the experiments; H.R.K. and K.H.L. analyzed the experimental data; C.W.L. supervised the project.

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Supplementary Materials
Figure S1: (a) scanning transmission electron microscopy of as-prepared SnO₂/ZC. Energy-dispersive X-ray spectroscopy mapping analysis of (b) O, (c) Sn, and (d) C. Figure S2: HRTEM image of the SnO₂/ZC catalyst under Ar/H₂ 300°C. Figure S3: particle diameter of (a) as-prepared, (b) 100°C, (c) 200°C, and (d) 300°C. Figure S4: plot of the formate partial current density of the SnO₂/ZC catalysts prepared with different annealing conditions. Figure S5: double-layer capacitance (Cdl) measurement of (a) as-prepared, (b) 100°C, (c) 200°C,
and (d) 300°C measured at -0.1 V to 0 V vs. Hg/HgO in 1 M KOH. Figure S6: H$_2$ FFs of the as-prepared SnO$_2$/ZC catalyst without PTFE (PTFE 0 wt%). Figure S7: in situ Raman spectroscopy of the as-prepared catalyst in a 0.5 M KHCO$_3$ solution. Table S1: previous reports on CO$_2$RR studies using the SnO$_2$ catalyst. Table S2: previous reports on CO$_2$RR studies using non-tin catalysts. (Supplementary Materials)

References

