Electronic Supplementary Information

A gradient Sn$^{4+}$(Sn$^{2+}$ core@shell structure induced by strong metal oxide-support interaction for enhanced CO$_2$ electroreduction

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Table S1. Comparison of CO$_2$RR performances of Sn-based catalysts for $C_1$ product.
1. Supplementary experiments

1.1 Preparation of g-C$_3$N$_4$ nanosheets

g-C$_3$N$_4$ nanosheets were synthesized according to a reported method with slight modifications. Typically, 6 g of urea was placed in crucible with a lid and annealed at 550 °C for 2 h with a ramping rate of 1 °C min$^{-1}$ under the flow of N$_2$ in a tube furnace. After cooling down to the room temperature, light yellow powders of g-C$_3$N$_4$ nanosheets were obtained.

1.2 Preparation of GO nanosheets

Graphite oxide (GO) nanosheets were fabricated according to a modified Hummer’ method. Firstly, an aqueous solution containing 180 mL of H$_2$SO$_4$ and 20 mL of H$_3$PO$_4$ was added to the powders of KMnO$_4$ (9.0 g) and graphite (1.5 g). The mixture was then stirred for 12 h. After cooling to room temperature, the suspension was mixed with an aqueous solution of H$_2$O$_2$ (30%) and a certain amount of ice. Then, the mixtures were centrifuged for 20 min with a rotation rate of 2000 rpm before being washed with water, concentrated hydrochloric acid solution and anhydrous ethyl ether at least twice. Finally, brownish GO nanosheets were collected after filtration using a polytetra fluoroethylene (PTFE) membrane with a pore size of 0.45 μm, followed by vacuum drying overnight at the ambient temperature.

2. Supplementary figures and tables
Fig. S1. SEM images of g-C$_3$N$_4$ (a) and GO (b) nanosheets.

Fig. S2. SEM (a), TEM (b) and HRTEM (c) images of SnO$_2$/rGO

Fig. S1 and S2 showed the morphologies and microstructures of g-C$_3$N$_4$, graphene oxide (GO) and SnO$_2$/rGO, respectively. Obviously, the surface of GO was slightly smoother than that of g-C$_3$N$_4$. During the hydrothermal process, GO was thermally converted to the reduced graphene oxide (rGO). Meanwhile, SnO$_2$ nanoparticles were grown on the rGO support homogeneously and densely via a hydrolysis-condensation process. The average particle size of SnO$_2$ NPs loaded on rGO was estimated to be about 5.0 nm (Fig. S2c), almost identical with the dimensional size of SnO$_2$ on g-C$_3$N$_4$ (4.8 nm). During the loading of tin oxides under the solvothermal conditions, the graphene oxide (GO) nanosheets were thermally reduced with the partial removal of oxygen-containing functional groups at the surfaces. As a result, the electrostatic repulsion between the functional groups was weakened and the reduced graphene oxide (rGO) nanosheets became destabilized. To resist the strain, the surfaces of rGO turned to be more folded spontaneously to achieve an equilibrium state with the lowest energy.
N\textsubscript{2} adsorption-desorption curves of the samples were measured at 77 K in a liquid nitrogen bath. SnO\textsubscript{2}/rGO showed slightly higher N\textsubscript{2} uptake than SnO\textsubscript{2}/g-C\textsubscript{3}N\textsubscript{4} (Fig. S4a). The BET surface areas were calculated to be 53.26 and 195.97 m\textsuperscript{2}/g for SnO\textsubscript{2}/g-C\textsubscript{3}N\textsubscript{4} and SnO\textsubscript{2}/rGO, respectively. Correspondingly, the pore size distributions were determined using the Barrett-Joyner-Halenda (BJH) method based on the adsorption branches. As can be seen from Fig. S4b-c, the pores of SnO\textsubscript{2}/g-C\textsubscript{3}N\textsubscript{4} and SnO\textsubscript{2}/rGO centered around 6.5 and 3.4 nm, respectively.
Fig. S4. FTIR spectra of g-C₃N₄, SnO₂/g-C₃N₄, GO, and SnO₂/rGO

For g-C₃N₄ (blue line) and SnO₂/g-C₃N₄ (red line), the broad peak from 3000 cm⁻¹ to 3700 cm⁻¹ corresponded to the stretching vibration of amine groups or water. The waves occurred between 1200 and 1700 cm⁻¹ were ascribed to CN heterocycles’ stretching and bending modes. The breathing mode of tri-s-triazine units showed up at about 810 cm⁻¹. Similarly, for GO (olive line) and SnO₂/rGO (black line), the broad peak from 3100 cm⁻¹ to 3700 cm⁻¹ was typical of the stretching vibration of the absorbed water molecules. The stretching vibration of C-O bond and sp² hybridized C=C bond occurred at about 1115 and 1620 cm⁻¹, respectively. The peak located around 1385 cm⁻¹ was assigned to the deformation mode of C-O-H. In all, the FTIR spectra showed no obvious differences between the substrates and the corresponding composites loaded with SnO₂ nanoparticles, indicating that the compositions and chemical groups were
well preserved during the hydrothermal synthesis process.

Fig. S5. $^1$H-NMR spectra of electrolytes after electrolysis at 1.06 V vs. RHE for 1 h under the CO$_2$ (a) and Ar (b) atmospheres over SnO$_2$/g-C$_3$N$_4$, respectively.
Fig. S6. Faradaic efficiencies of HCOOH (a, c) and CO (b, d) for SnO$_2$/g-C$_3$N$_4$ and SnO$_2$/rGO at different potentials.

The liquid and gas products during electrolysis were detected by the $^1$H-NMR (Fig. S5) and GC spectra (Fig. S7), respectively. The FEs of HCOOH for SnO$_2$/g-C$_3$N$_4$ (19.3-80.2%) electrode were significantly higher than that for SnO$_2$/rGO (3.9-50.0%) (Fig. S6a, c). In contrast, the difference of the CO generating ability of the two catalysts was not that big (Fig. S6b, d). Both catalysts exhibited volcano-like trends between CO FEs and the potentials. For SnO$_2$/g-C$_3$N$_4$, the values ranged from 11.8% to 28.7%, whereas for SnO$_2$/rGO, the values varied from 12.6% to 21.9%. Overall, the former showed slightly higher selectivity toward CO than the latter.

Fig. S7. GC spectra of the gas products of CO and H$_2$ detected by the FID and TCD after electrolysis at 1.06 V vs. RHE for 1 h under the atmosphere of CO$_2$ or Ar. For comparison, the feeding gas of Ar was directly purged into the GC. It can be observed that trace amounts of CO and H$_2$ were present in the feeding Ar gas.
Fig. S8. 3D color pie chart for the faradaic efficiencies of H$_2$, HCOOH and CO after electrolysis at -1.06 V vs. RHE for 1 h under the atmosphere of Ar.

Fig. S9 Potential-dependent energy efficiencies for converting CO$_2$ into HCOOH over SnO$_2$/g-C$_3$N$_4$ (a) and SnO$_2$-rGO (b).
The ECSA of SnO$_2$/g-C$_3$N$_4$, SnO$_2$/rGO and commercial SnO$_2$ were evaluated based on the double-layer capacitances ($C_{dl}$) (Fig. S10). Obviously, the value of $C_{dl}$ for SnO$_2$/rGO (59.5 mF cm$^{-2}$) was almost two and six times that of SnO$_2$/g-C$_3$N$_4$ (32.9 mF cm$^{-2}$) and commercial SnO$_2$ (10.8 mF cm$^{-2}$), respectively. As shown in Fig. S11, after normalization to the double-layer capacitance, the partial current densities of C1 products for SnO$_2$/g-C$_3$N$_4$ were higher than those of SnO$_2$/rGO over the entire potential range. Specifically, the value for SnO$_2$/g-C$_3$N$_4$ (0.29 mA mF$^{-1}$) is about four times that for SnO$_2$/rGO (0.07 mA mF$^{-1}$) at -1.36 V.
Fig. S11. Normalized $C_1$ partial current densities for SnO$_2$/g-C$_3$N$_4$ and SnO$_2$/rGO.

![Graph showing normalized $j_{C_1}$ vs. potential (V vs. RHE).]

Fig. S12. (a) XRD pattern, (b) SEM and (c) TEM images of commercial SnO$_2$.

The typical diffraction peaks of commercial SnO$_2$ match well with the tetragonal SnO$_2$ (PDF #41-1445) (Fig. S12 a). SEM and TEM images indicate the uniformity of the SnO$_2$ NPs (Fig. S12 b, c). The differences in LSV curves taken under Ar and CO$_2$-saturated 0.1 M KHCO$_3$ solutions suggest that the commercial SnO$_2$ is also active for CO$_2$RR (Fig. S13 a). Product analysis shows that the FE of HCOOH varies from 13.2% to 71.3%. Meanwhile, the FE of $C_1$ products increases from 13.2% to 89.1%. The CO$_2$RR performances of commercial SnO$_2$ were superior to those of SnO$_2$/rGO but inferior to SnO$_2$/g-C$_3$N$_4$. 
Fig. S13. LSV curves in Ar- and CO$_2$-saturated 0.1 M KHCO$_3$ (a) and the corresponding FEs of H$_2$, CO and HCOOH over commercial SnO$_2$.

Fig. S14 Faradaic efficiencies of C1 products (a) and H$_2$ (b) at different potentials over SnO$_2$/g-C$_3$N$_4$, SnO$_2$/rGO and commercial SnO$_2$.

The CO$_2$RR performances of commercial SnO$_2$ were also investigated (Fig. S13 and S14). The faradaic efficiencies of C1 products and H$_2$ at different potentials over SnO$_2$/g-C$_3$N$_4$, SnO$_2$/rGO and commercial SnO$_2$ were compared in Fig. S14. In terms of faradaic efficiencies of C1 products, SnO$_2$/g-C$_3$N$_4$ took obvious advantage over commercial SnO$_2$ at potentials more negative than -0.66 V. The maximum difference between the two samples reached about 13%. At potentials more positive than -0.66 V, they exhibited similar selectivity for C1 products. Noticeably, both were superior to the sample of SnO$_2$/rGO in producing C1 products from CO$_2$RR. The performance distinctions between the three samples further highlighted the importance of the metal oxide-support interaction in improving the catalytic properties.
The survey XPS results indicate the presence of Sn and O in commercial SnO$_2$. The high-resolution Sn 3d XPS spectra show the Sn$_{3/2}$ and Sn$_{5/2}$ peak are located at 495.6 and 487.2 eV, respectively. Noticeably, the bivalent Sn$^{2+}$ takes up 77% of the total surface Sn species. By careful comparison, we found that the FEs for HCOOH or C$_1$ product showed an increasing trend with the decrease of the binding energy of Sn 3d$_{3/2}$ from 496.0 to 495.6 to 495.0 eV, implying that the chemical state of Sn species in the catalysts had significant impact on the CO$_2$RR performances.

![Fig. S15](image1.png)

**Fig. S15.** Survey (a), Sn 3d (b) and O 1s spectra (c) of commercial SnO$_2$.

![Fig. S16](image2.png)

**Fig. S16.** Regular core-level Sn 3d XPS and depth profiles with 30 s Ar sputtering for SnO$_2$/g-C$_3$N$_4$ after reaction.
As can be seen from the Nyquist plots in Fig. S17, the charge transfer resistance increased from SnO$_2$/rGO to commercial SnO$_2$ and to SnO$_2$/g-C$_3$N$_4$. Noticeably, the value of the commercial SnO$_2$ lied in between that of SnO$_2$/rGO and SnO$_2$/g-C$_3$N$_4$. The smaller resistance for SnO$_2$/rGO compared with SnO$_2$/g-C$_3$N$_4$ might originate from the inherently higher electrical conductivity of rGO. Even though, SnO$_2$/g-C$_3$N$_4$ still delivered a higher partial current density of C$_1$ products, further confirming the intrinsic structural superiority of SnO$_2$/g-C$_3$N$_4$ in CO$_2$RR.
### Table S1. Comparison of CO$_2$RR properties of Sn-based catalysts for C$_1$ product.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Electrolyte</th>
<th>Potential (V vs. RHE)</th>
<th>FE$_{C1}$ (%)</th>
<th>Stability (h)</th>
<th>Ref.</th>
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<td>Sn/CP-UPED</td>
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<td>-1.16</td>
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<tr>
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References