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## Electrochemical conversion of $\text{CO}_2$ into $\text{HCOO}^-$ in a synergistic manner by a nanocomposite of $\text{Zn}_2\text{SnO}_4/\text{ZnO}$

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Exploring environmentally friendly nanomaterials as alternatives to toxic metals for electrocatalytic  $\text{CO}_2$  reduction into formate is very important. Designing a nanocomposite catalyst with different phase components is an underlying strategy to achieve prominent catalysts for electrochemical  $\text{CO}_2$  reduction owing to the potential capacity to regulate electronic structure by interfacial interactions. Herein, we report a novel nanocomposite with components of cubic-like  $\text{Zn}_2\text{SnO}_4$  and nanosheet-structured  $\text{ZnO}$  ( $\text{Zn}_2\text{SnO}_4/\text{ZnO}$ ) as an efficient electrocatalyst for the  $\text{CO}_2$  reduction reaction (CO<sub>2</sub>RR). This strategy can reduce the use of toxic metals and the cost of the catalyst. The composite exhibited a maximum faradaic efficiency (FE) of 98% for the  $\text{C}_1$  product, and even approached 90% for formate production at  $-1.0$  V *versus* the reversible hydrogen electrode, along with excellent durability. In contrast, the maximum FE<sub>HCOOH</sub> of a single  $\text{ZnO}$  component or  $\text{Zn}_2\text{SnO}_4$  component were both  $<50\%$  over the potential window. Coupling of X-ray photoelectron/adsorption spectroscopy and electrochemical measurements revealed interfacial charge transfer and oxygen vacancies to result in an optimized electronic structure of  $\text{Zn}_2\text{SnO}_4/\text{ZnO}$ . This was favorable for an  $\text{HCOO}^*$  intermediate-involved reaction pathway, together with an enlarged electrochemical active area, which boosted the selectivity and activity of formate synergistically.

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## Introduction

The rapid rising of the carbon dioxide level in the Earth's atmosphere has caused serious climate change and subsequent chain reactions.<sup>1–5</sup> Methods usually employed for  $\text{CO}_2$  conversion include thermal catalysis, photocatalysis, and electrocatalysis. Among these methods, electrocatalytic  $\text{CO}_2$  reduction to valuable fuels and chemicals powered by renewable energy resources can alleviate environmental issues effectively, but also realize the recycling of energy, thereby attracting great interest.<sup>6,7</sup> The products of an electrochemical  $\text{CO}_2$  reduction reaction (CO<sub>2</sub>RR) are diverse: CO, HCOOH, CH<sub>4</sub>, C<sub>2</sub>H<sub>5</sub>OH, C<sub>2</sub>H<sub>4</sub>, and C<sub>2</sub>H<sub>6</sub>.<sup>8,9</sup> Among them, HCOOH is considered to be a crucial raw material for basic organic chemicals

that is commonly applied in food additives, printing, and dyeing.<sup>10</sup> Formate is a potential choice for storing and delivering liquid hydrogen. Formate can release H<sub>2</sub> if needed, and can be used as a chemical fuel for direct formate fuel cells. Besides, as a liquid product, formate can be stored and transported readily, and saves the cost of liquefaction processes compared with gas products. Thus, formate presents the highest net value and is economically competitive if evaluated from a technoeconomic aspect.<sup>11</sup> However,  $\text{CO}_2$  electroreduction to formate is hindered due to the high chemical inertness of  $\text{CO}_2$  (bond energy = 806 kJ mol<sup>-1</sup>), so a high overpotential is needed for activation.<sup>12</sup> In addition, CO<sub>2</sub>RR involves competition from multiple reaction paths and is usually accompanied by other competitive side reactions, especially the hydrogen-evolution reaction (HER). Even though considerable effort has been devoted to promoting formate production, many problems are encountered, such as a low conversion rate and poor selectivity. Therefore, developing high-performance electrocatalysts to facilitate the  $\text{CO}_2$ -to-formate conversion is highly desired, but challenging.

Some metals and their oxides electrodes, such as Pb,<sup>13</sup> Bi,<sup>14</sup> Sn,<sup>15</sup> and In,<sup>16</sup> possess relatively high selectivity towards  $\text{CO}_2$  reduction to formate. However, the expense of Pd, as well as the toxicity and environmental unfriendliness of In and Pd,

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makes them unsuitable for large-scale application. Hence, catalysts composed of elements characterized by high abundance and nontoxicity have garnered more attention. Recently, zinc-based catalysts have aroused wide interest due to the low cost, nontoxicity, and capacity for electrocatalytic  $\text{CO}_2$  reduction.<sup>17-19</sup> For example, a  $\text{ZnO}$  sheet array supported on  $\text{Zn}$  foil showed a high faradaic efficiency (FE) of 85% for  $\text{CO}_2$ RR to  $\text{CO}$  at  $-2.0$  V (vs.  $\text{Ag}/\text{AgCl}$ ).<sup>20</sup> Moreover,  $\text{Ce}_{0.016}\text{Zn}_{0.984}\text{O}$  exhibited a maximum  $\text{FE}_{\text{CO}}$  of 88% at  $-1.0$  V vs. the reversible hydrogen electrode (RHE) and excellent stability for continuous testing.<sup>21</sup> Hence,  $\text{Zn}$ -based catalysts tend to electrocatalyze the reduction of  $\text{CO}_2$  to  $\text{CO}$ . Can the selectivity of  $\text{ZnO}$  be changed from  $\text{CO}$  to formate by dual engineering of electronic structure and morphology? In general, the precise manipulation of a component, morphology and size is an effective method to regulate the energy efficiency and selectivity for  $\text{CO}_2$ RR by the “electronic effect” and “geometric effect”.<sup>22</sup>

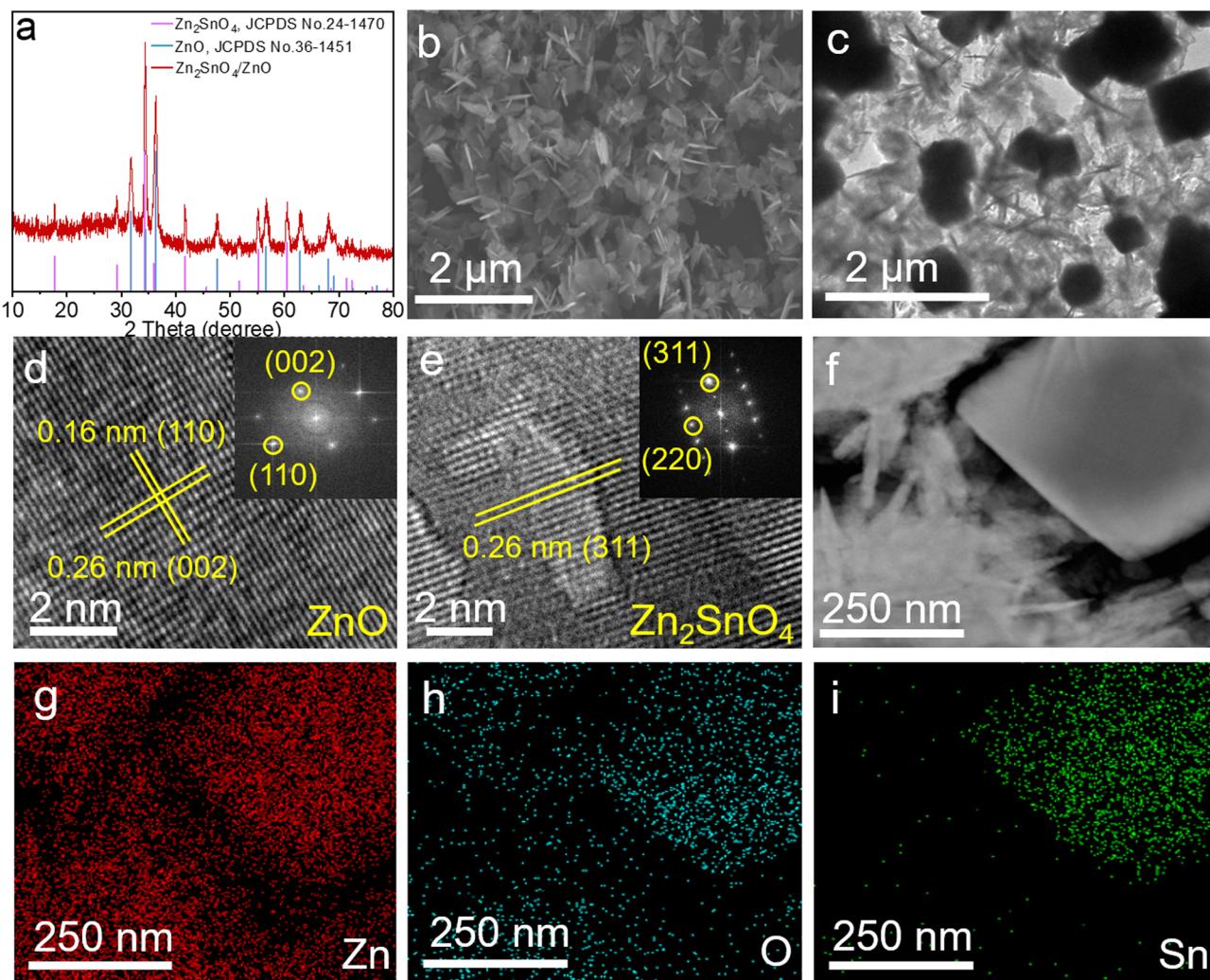
Creation of heterostructures with different components affords a feasible approach for engineering the  $\text{CO}_2$ RR performance by “tuning” the electronic structure.<sup>12,23</sup> Due to a strong interaction at the interface,  $\text{CuO}/\text{In}_2\text{O}_3$  composites enable remarkable electroreduction activity of  $\text{CO}_2$  to  $\text{CO}$  with a  $\text{FE}_{\text{CO}}$  of 93.0% at  $-0.7$  vs. RHE.<sup>24</sup> Guan and co-workers<sup>25</sup> reported that  $\text{SnO}_2/\text{ZnO}$  composites exhibited enhanced performance of  $\text{CO}_2$ -to- $\text{HCOO}^-$  conversion with a maximum  $\text{FE}_{\text{HCOO}^-}$  of 76.70% at  $-1.16$  V vs. RHE. Interfacial charge transport is enhanced in  $\text{Zn}_2\text{SnO}_4/\text{SnO}_2$  heterostructures, which greatly reduces the kinetic barriers of  $\text{CO}_2$ RR and results in excellent selectivity for  $\text{HCOOH}$ .<sup>12</sup> In addition, nanostructuring of composite catalysts would create preferential faceting, vacancy defects and more unsaturated coordination sites, thereby tuning their electronic structure as well as the binding energy of key intermediates.<sup>26</sup>

Herein, we developed an effective strategy for promoting  $\text{CO}_2$  electroreduction to formate by constructing a nanocomposite catalyst with  $\text{Zn}_2\text{SnO}_4$  and  $\text{ZnO}$  phase components. With low Sn content of 6.65 wt%, the resultant  $\text{Zn}_2\text{SnO}_4/\text{ZnO}$  composite catalyst with oxygen vacancies exhibited greatly enhanced activity and selectivity for electrochemical  $\text{CO}_2$  reduction to formate, with a maximum  $\text{FE}_{\text{HCOOH}}$  of 87% at  $-1.0$  V vs. RHE and a larger partial current density of formate ( $46$  mA  $\text{cm}^{-2}$ ), which was markedly superior to those of a single  $\text{ZnO}$  component or  $\text{Zn}_2\text{SnO}_4$  component. Based on experimental analyses, the improved catalytic performance could be ascribed to three aspects. The first was a cubic-like structured  $\text{Zn}_2\text{SnO}_4$  and nanosheet-structured  $\text{ZnO}$  that enabled intimate contact with each other, providing abundant  $\text{ZnO-Zn}_2\text{SnO}_4$  heterostructure interfaces, promoting charge redistribution and altering the electronic structure. Second, the nanostructured hybrids were beneficial for mass transport and enlarged the contact between reaction intermediates and the  $\text{Zn}_2\text{SnO}_4/\text{ZnO}$  catalyst. Third, the optimized electronic properties were in favour of a  $\text{HCOO}^*$  intermediate-involved reaction pathway (Fig. S1†), and thereby enhanced the selectivity of formate. This work highlights the design of composite electrocatalysts to render excellent catalytic performance by intimate interface interaction.

## Results and discussion

A facile one-step hydrothermal method was applied to prepare the  $\text{Zn}_2\text{SnO}_4/\text{ZnO}$  composite catalyst. As displayed by the X-ray diffraction (XRD) pattern in Fig. 1a, all the peaks closely matched the main characteristic peaks of hexagonal-phase  $\text{ZnO}$  with a  $P63mc(186)$  space group (JCPDS number: 36-1451)<sup>27</sup> and cubic-phase  $\text{Zn}_2\text{SnO}_4$  (JCPDS number: 24-1470).<sup>28</sup> Compared with pristine  $\text{ZnO}$ , the diffraction peaks of  $\text{ZnO}$  in  $\text{Zn}_2\text{SnO}_4/\text{ZnO}$  composite showed a slight shift towards a high diffraction angle (Fig. S2†), thereby demonstrating the strong interaction between  $\text{ZnO}$  and  $\text{Zn}_2\text{SnO}_4$ . This interaction may result in compressive strain in a composite catalyst and be favourable for reducing the energy barrier of  $\text{HCOOH}$  production, especially the potential-limiting step.<sup>29</sup> The scanning electron microscope (SEM) image of the  $\text{Zn}_2\text{SnO}_4/\text{ZnO}$  catalyst is shown in Fig. 1b. It demonstrates the coexistence of a nanosheet and nano-cube in  $\text{Zn}_2\text{SnO}_4/\text{ZnO}$ , which was further confirmed by the transmission electron microscopy (TEM) image in Fig. 1c. As evidenced by a high-angle annular dark field (HAADF)-STEM image and corresponding elemental mappings in Fig. 1f-i, the component in  $\text{Zn}_2\text{SnO}_4/\text{ZnO}$  with nanosheet morphology was  $\text{ZnO}$ , whereas  $\text{Zn}_2\text{SnO}_4$  was cubic. The thickness of the  $\text{ZnO}$  nanosheet was  $\sim 20$  nm, and resulted in more exposed active sites and increased the carrier density of the catalyst.<sup>30</sup> Furthermore, the  $\text{ZnO}$  in  $\text{Zn}_2\text{SnO}_4/\text{ZnO}$  composite had a rough surface with many pore structures, which greatly improved the mass transfer rate of the catalyst (Fig. S3†). Fig. 1d shows the high-resolution TEM (HRTEM) image of the  $\text{ZnO}$  constituent. The clear lattice fringes with interlayer spacings of  $0.16$  nm and  $0.26$  nm were assigned to the (100) and (002) planes of  $\text{ZnO}$ , respectively. The inset of Fig. 1d shows the corresponding FFT image, which distinctly shows a single-crystal structure with excellent crystallinity. The HRTEM image and corresponding FFT pattern of the  $\text{Zn}_2\text{SnO}_4$  constituent are displayed in Fig. 1e. The clear lattice spacing of  $0.26$  nm was assigned to the (311) planes of  $\text{Zn}_2\text{SnO}_4$  with a  $Fd\bar{3}m$  space group. Inductively coupled plasma-optical emission spectrometry (ICP-OES) revealed a relatively low Sn content of  $\sim 6.65$  wt% in the composite. Evidently, the  $\text{Zn}_2\text{SnO}_4/\text{ZnO}$  composite had been synthesized successfully. To show the great advantage of forming a composite for electrochemical  $\text{CO}_2$  reduction, pristine  $\text{ZnO}$  and  $\text{Zn}_2\text{SnO}_4$  were also prepared by a one-step hydrothermal method. The XRD patterns in Fig. S4 and 5† demonstrate the phases of the prepared reference materials to be hexagonal-phase  $\text{ZnO}$  and cubic-phase  $\text{Zn}_2\text{SnO}_4$ . Fig. S6† shows the SEM image of synthesized  $\text{ZnO}$ . Accordingly, the  $\text{ZnO}$  catalyst exhibited a nanosheet morphology with a similar thickness to that in the  $\text{Zn}_2\text{SnO}_4/\text{ZnO}$  composite, which increased the number of exposed active sites for  $\text{CO}_2$ RR.

To gain deep insight into the coordination environment and electronic state of the  $\text{Zn}_2\text{SnO}_4/\text{ZnO}$  catalyst, X-ray photo-electron spectroscopy (XPS), X-ray absorption near-edge structure spectroscopy (XANES), and extended X-ray absorption fine structure (EXAFS) spectroscopy were carried out. The XPS survey spectrum in Fig. 2a shows the constituent elements of

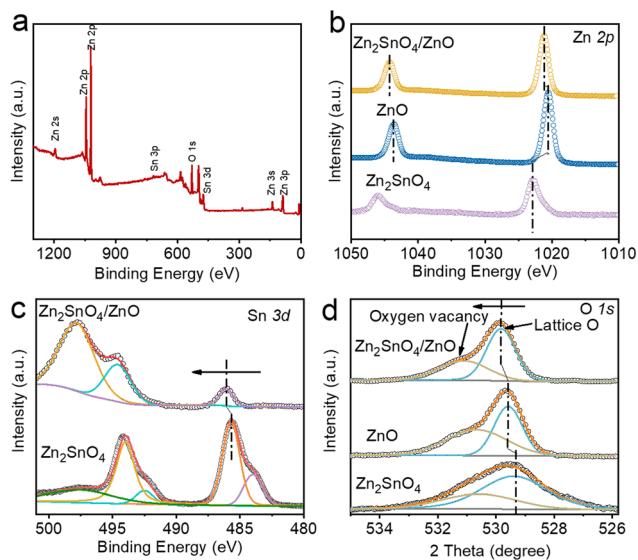


**Fig. 1** (a) XRD pattern of Zn<sub>2</sub>SnO<sub>4</sub>/ZnO. (b) SEM image of Zn<sub>2</sub>SnO<sub>4</sub>/ZnO. (c) TEM image of Zn<sub>2</sub>SnO<sub>4</sub>/ZnO. (d) HRTEM image and corresponding FFT pattern of the ZnO constituent. (e) HRTEM image and corresponding FFT pattern of the Zn<sub>2</sub>SnO<sub>4</sub> constituent. (f) STEM of Zn<sub>2</sub>SnO<sub>4</sub>/ZnO. (g–i) EDS mapping of Zn, O and Sn.

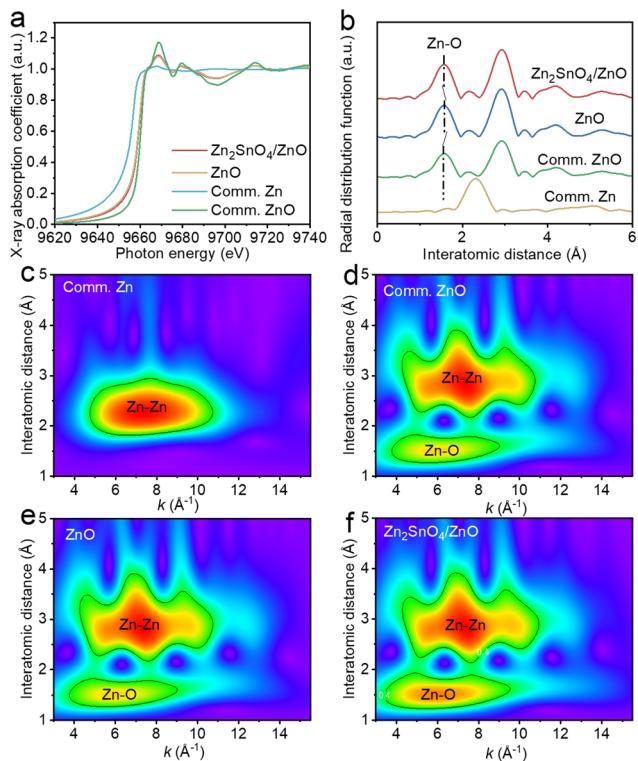
Zn, Sn, and O in Zn<sub>2</sub>SnO<sub>4</sub>/ZnO, which was in agreement with the elemental mapping results stated above. The Zn 2p spectrum of ZnO exhibited two symmetrical peaks of Zn 2p<sub>3/2</sub> and Zn 2p<sub>1/2</sub> at 1020.6 and 1043.8 eV, respectively (Fig. 2b).<sup>31</sup> The two peaks corresponding to Zn 2p<sub>3/2</sub> and 2p<sub>1/2</sub> of Zn<sub>2</sub>SnO<sub>4</sub> were located at 1022.8 eV and 1045.9 eV. The two relative peaks in Zn<sub>2</sub>SnO<sub>4</sub>/ZnO were positioned at 1021.19 and 1044.28 eV, respectively. These results demonstrated that the valence of Zn in the Zn<sub>2</sub>SnO<sub>4</sub>/ZnO composite had been optimized, and lay between that of pristine Zn<sub>2</sub>SnO<sub>4</sub> and ZnO, and perhaps contributed to the enhanced activity and selectivity towards CO<sub>2</sub> electroreduction to formate. Fig. 2c shows the Sn 3d XPS spectra of Zn<sub>2</sub>SnO<sub>4</sub>/ZnO and Zn<sub>2</sub>SnO<sub>4</sub>. In the case of Zn<sub>2</sub>SnO<sub>4</sub>, the two main peaks with binding energies of 494.2 eV and 485.6 eV belonged to the Sn 3d<sub>3/2</sub> and Sn 3d<sub>5/2</sub> of Sn<sup>4+</sup>.<sup>32</sup> Two smaller peaks at 492.5 eV and 484.0 eV were ascribed to the small amount of metallic Sn.<sup>33</sup> When forming a composite with ZnO, both of these two peaks of Sn 3d<sub>3/2</sub> and Sn 3d<sub>5/2</sub> of

Sn<sup>4+</sup> showed a slight shift towards high binding energies and were located at 494.7 and 486.1 eV, respectively, thereby indicating electron depletion around Sn atoms.<sup>32</sup> In the high-resolution O 1s spectrum of Zn<sub>2</sub>SnO<sub>4</sub>, two peaks centered at 529.3 eV and 530.5 eV were attributed to the coordination of O in Sn–O–Sn and Sn–O–Zn, respectively (Fig. 2d).<sup>12</sup> For ZnO, two peaks with binding energies of 529.9 and 531.3 eV could be observed in the O 1s spectrum, and were attributed to lattice O and oxygen vacancies (O<sub>v</sub>).<sup>34</sup> When forming Zn<sub>2</sub>SnO<sub>4</sub>/ZnO composite materials, the peaks related to O<sub>v</sub> and lattice O shifted to high binding energies, which demonstrated the charge redistribution in a composite system. These O<sub>v</sub> defects play an important part in increasing the selectivity of formate and the active sites of CO<sub>2</sub>RR.<sup>35,36</sup> Furthermore, the H\* adsorption free energy could be weakened by O<sub>v</sub> and, thus, inhibit the HER side reaction.<sup>37–39</sup>

Fig. 3a displays the Zn K-edge XANES spectrum of Zn<sub>2</sub>SnO<sub>4</sub>/ZnO compared with prepared ZnO, commercial ZnO (Comm.



**Fig. 2** Characterizations of electronic structure. (a) XPS survey spectrum of  $\text{Zn}_2\text{SnO}_4/\text{ZnO}$ . (b) High-resolution Zn 2p XPS spectra of  $\text{Zn}_2\text{SnO}_4/\text{ZnO}$ , ZnO and  $\text{Zn}_2\text{SnO}_4$ . (c) High-resolution Sn 3d XPS spectra of  $\text{Zn}_2\text{SnO}_4/\text{ZnO}$  and  $\text{Zn}_2\text{SnO}_4$ . (d) High-resolution O 1s XPS spectra of  $\text{Zn}_2\text{SnO}_4/\text{ZnO}$ , ZnO and  $\text{Zn}_2\text{SnO}_4$ .



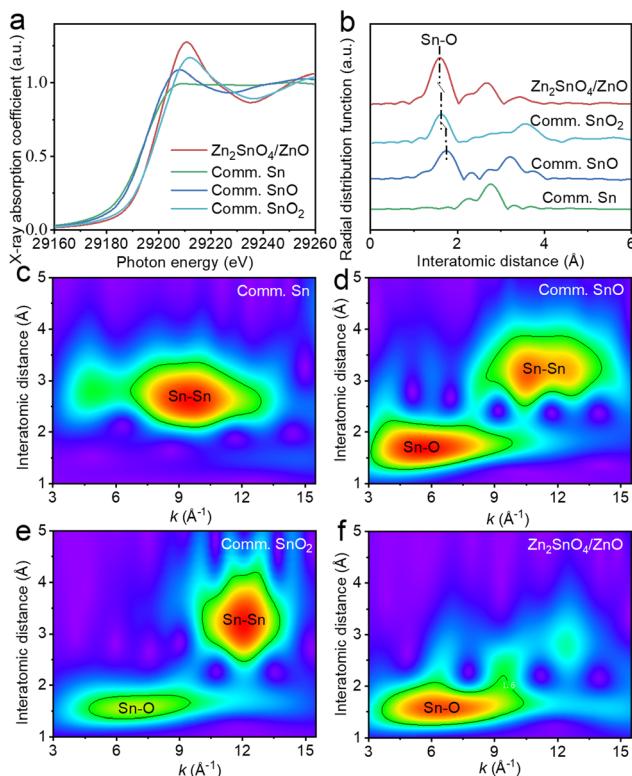
**Fig. 3** (a) Zn K-edge XANES and (b)  $k^3$ -weighted FT-EXAFS spectra of ZnO,  $\text{Zn}_2\text{SnO}_4/\text{ZnO}$  and reference materials. WT analysis of (c) Comm. Zn, (d) Comm. ZnO, (e) ZnO and (f)  $\text{Zn}_2\text{SnO}_4/\text{ZnO}$ .

ZnO), and commercial Zn (Comm. Zn). In the case of prepared ZnO, the main absorption peak at 9668 eV and anterior resonance peak of 9683 eV are typical features of hexagonal-phase

ZnO.<sup>35</sup> However, its pre-edge adsorption exhibited an obvious negative shift in comparison with that of Comm. ZnO, thereby demonstrating the lower oxidation state of Zn in prepared ZnO.<sup>36</sup> Meanwhile, the pre-edge adsorption of  $\text{Zn}_2\text{SnO}_4/\text{ZnO}$  had a slightly positive shift compared with that of prepared ZnO, but lower than that of Comm. ZnO, implying that the valence state of Zn in formed  $\text{Zn}_2\text{SnO}_4/\text{ZnO}$  was lower than +2. The Fourier transform (FT) spectra of  $\text{Zn}_2\text{SnO}_4/\text{ZnO}$  and reference samples are shown in Fig. 3b. The first coordination shell in prepared ZnO had Zn–O coordination with a scattering peak at 1.58 Å, which was right-shifted by 0.02 Å compared with that in Comm. ZnO, and demonstrated an elongated Zn–O bond in prepared ZnO compared with that in Comm. ZnO. However, the peak associated with Zn–O coordination was located at 1.57 Å for  $\text{Zn}_2\text{SnO}_4/\text{ZnO}$ . This value was larger than that of Comm. ZnO but smaller than that of prepared ZnO, which indicated the charge redistribution of the  $\text{Zn}_2\text{SnO}_4/\text{ZnO}$  composite. To further study the changes in valence state and electronic structure,  $R$  and  $k$  space-involved wavelet transform (WT) analyses were undertaken. The WT EXAFS contour plots of Comm. ZnO, Comm. Zn, prepared ZnO and  $\text{Zn}_2\text{SnO}_4/\text{ZnO}$  are shown in Fig. 3c–f. The WT plots of  $\text{Zn}_2\text{SnO}_4/\text{ZnO}$  showed two maxima at 6.27 Å<sup>-1</sup> and 7.38 Å<sup>-1</sup>, which belonged to Zn–O and Zn–Zn co-ordinations, respectively. The intensity and  $k$ -value of the two backscattering paths were similar to those of Comm. ZnO and prepared ZnO, implying the same structural order.

The Sn K-edge XANES spectra of  $\text{Zn}_2\text{SnO}_4/\text{ZnO}$  and commercial references are displayed in Fig. 4a. The higher maximum adsorption of  $\text{Zn}_2\text{SnO}_4/\text{ZnO}$  than that of commercial  $\text{SnO}_2$  (Comm.  $\text{SnO}_2$ ) demonstrated the higher degree of structural distortion.<sup>40</sup> Moreover, the slightly right-shifted white-line peak of  $\text{Zn}_2\text{SnO}_4/\text{ZnO}$  compared with Comm.  $\text{SnO}_2$  demonstrated the lower electron density of Sn in the composite. Fig. 4b illustrates the FT-EXAFS spectra of  $\text{Zn}_2\text{SnO}_4/\text{ZnO}$ , Comm.  $\text{SnO}_2$ , Sn and SnO. For Comm.  $\text{SnO}_2$ , two scattering peaks related to Sn–O and Sn–Sn were detected. The spectrum of  $\text{Zn}_2\text{SnO}_4/\text{ZnO}$  displayed a dominant peak at 1.59 Å (attributed to a Sn–O interaction) and a lower-intensity peak at 3.43 Å (corresponding to a Sn–Sn interaction). Both peaks were negative-shifted relative to those of Comm.  $\text{SnO}_2$ . Besides, a new peak appeared at 2.69 Å for  $\text{Zn}_2\text{SnO}_4/\text{ZnO}$ , which could be assigned to a Sn–Zn interaction.<sup>41</sup> A maximum at 6.6 Å<sup>-1</sup> was observed in the WT plots of  $\text{Zn}_2\text{SnO}_4/\text{ZnO}$ , which corresponded to the Sn–O interaction compared with the references Comm.  $\text{SnO}_2$ , SnO and Sn foil (Fig. 4c–f). The  $k$ -value of the Sn–O path in  $\text{Zn}_2\text{SnO}_4/\text{ZnO}$  was similar to that of Comm.  $\text{SnO}_2$ , but the intensity was greater.

The CO<sub>2</sub>RR performance of  $\text{Zn}_2\text{SnO}_4/\text{ZnO}$  composite was investigated in a flow cell using a three electrode system (Fig. S7†). The performance of pristine  $\text{Zn}_2\text{SnO}_4$  and ZnO was also evaluated as references. The linear sweep voltammetry (LSV) curves of  $\text{Zn}_2\text{SnO}_4/\text{ZnO}$ , ZnO and  $\text{Zn}_2\text{SnO}_4$  in CO<sub>2</sub>-saturated and Ar-saturated 0.5 M KHCO<sub>3</sub> electrolyte are displayed in Fig. S8.† All three catalysts exhibited enhanced current density in the CO<sub>2</sub>-saturated electrolyte than in the Ar-satu-



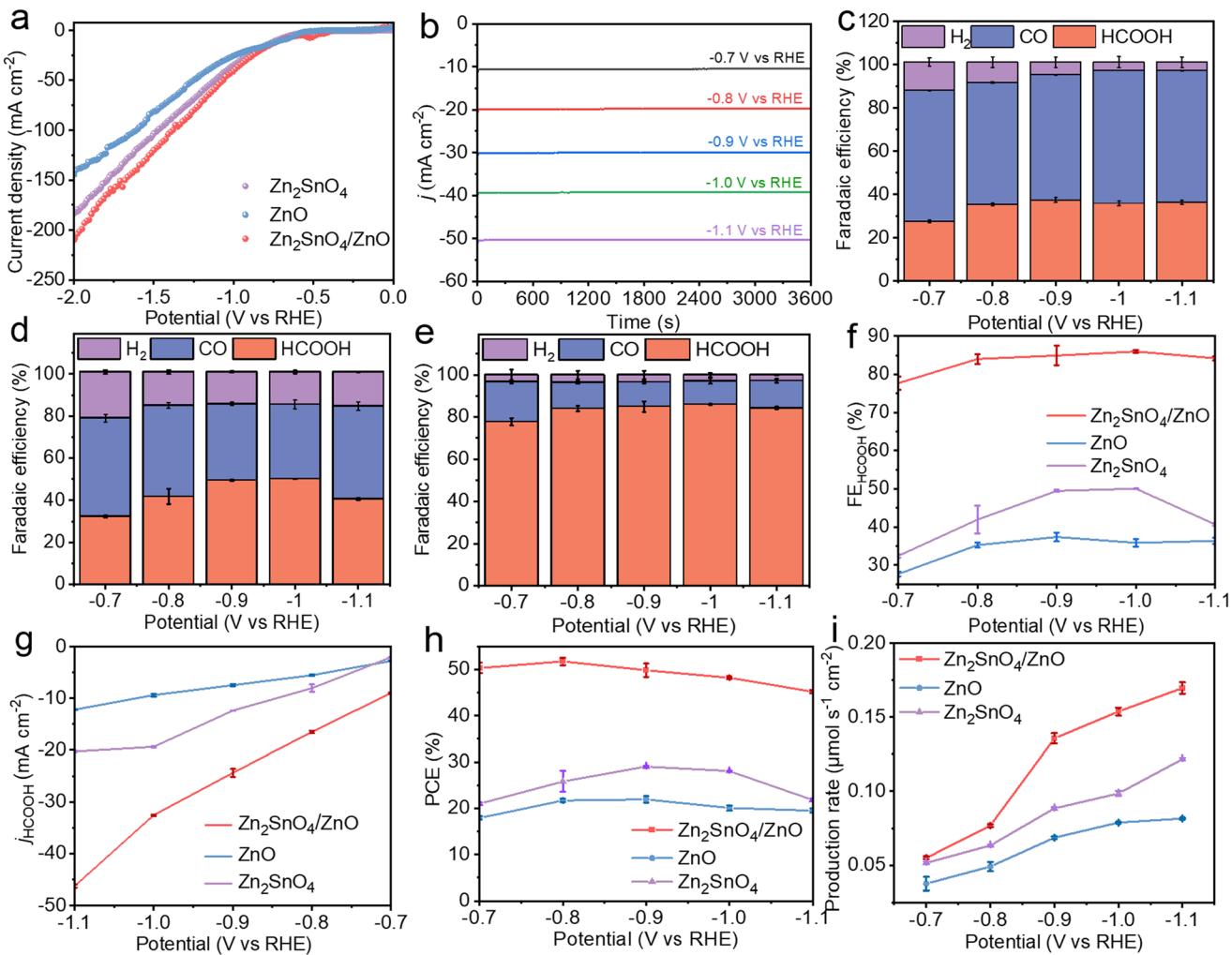
**Fig. 4** (a) Sn K-edge XANES and (b)  $k^3$ -weighted FT-EXAFS spectra of  $\text{Zn}_2\text{SnO}_4/\text{ZnO}$  and reference materials. WT analysis of (c) Comm. Sn, (d) Comm. SnO, (e) Comm. SnO<sub>2</sub> and (f)  $\text{Zn}_2\text{SnO}_4/\text{ZnO}$ .

rated electrolyte. More importantly, the current density of  $\text{Zn}_2\text{SnO}_4/\text{ZnO}$  in  $\text{CO}_2$ -saturated solution was greater than that of pristine  $\text{ZnO}$  and  $\text{Zn}_2\text{SnO}_4$  (Fig. 5a), which demonstrated the enhanced activity of a composite catalyst towards  $\text{CO}_2$  reduction. The products of  $\text{CO}_2$ RR on  $\text{Zn}_2\text{SnO}_4/\text{ZnO}$  and reference catalysts were evaluated after continuous electrochemical measurement for 1 h under different potentials (Fig. 5b). Gas products were quantified *via* on-line gas chromatography (Fig. S9†). Liquid products were measured by <sup>1</sup>H nuclear magnetic resonance (NMR) spectroscopy (Fig. S10†). Fig. 5c shows that synthetic  $\text{ZnO}$  exhibited selectivity for formate production with a maximum faradaic efficiency (FE) of 38% at an applied potential of  $-0.9$  V vs. RHE, which is high selectivity for a  $\text{ZnO}$ -based catalyst for  $\text{HCOOH}$  production compared with that reported previously. This result could be attributed to oxygen vacancies enhancing  $\text{CO}_2$  adsorption and two-dimensional nanosheet morphology, which leads to special crystal orientation. Even so, CO was the main product of  $\text{CO}_2$ RR on a  $\text{ZnO}$  catalyst with FE >60% at all applied potentials. In the case of  $\text{Zn}_2\text{SnO}_4$ , the main product of  $\text{CO}_2$ RR was  $\text{HCOOH}$ , but  $\text{FE}_{\text{HCOOH}}$  was <50% over all applied potentials (Fig. 5d). The  $\text{FE}_{\text{CO}}$  and  $\text{FE}_{\text{H}_2}$  for  $\text{Zn}_2\text{SnO}_4$  are displayed in Fig. S11†. Upon formation of a composite,  $\text{Zn}_2\text{SnO}_4/\text{ZnO}$  exhibited greatly enhanced selectivity for formate with a maximum  $\text{FE}_{\text{HCOOH}}$  of 87% at  $-1.0$  V vs. RHE. Moreover, the  $\text{FE}_{\text{HCOOH}}$  of  $\text{Zn}_2\text{SnO}_4/\text{ZnO}$  was maintained at >80% at a wide potential window ( $-0.8$

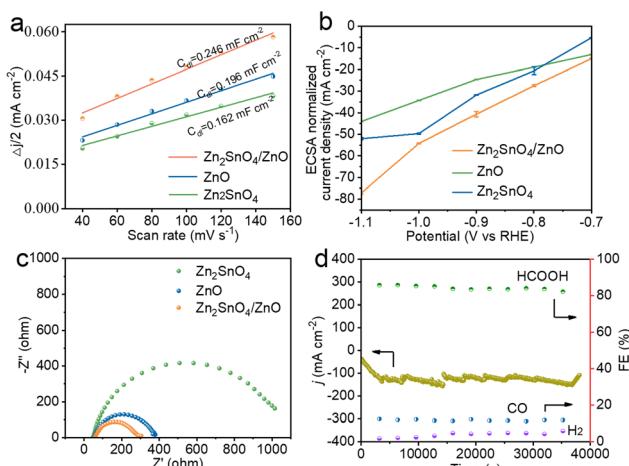
V to  $-1.1$  V vs. RHE) (Fig. 5e and f). The total  $\text{C}_1$  products, including CO and formate, was >97% for  $\text{Zn}_2\text{SnO}_4/\text{ZnO}$  over a potential window of  $-0.8$  V to  $-1.1$  V vs. RHE (Fig. S11†), thereby demonstrating a strong capacity for suppressing the HER.

$\text{Zn}_2\text{SnO}_4/\text{ZnO}$  exhibited excellent performance towards  $\text{HCOOH}$  production in comparison with single  $\text{ZnO}$  and  $\text{Zn}_2\text{SnO}_4$ , which corroborated the advantages of a synergistic effect in  $\text{Zn}_2\text{SnO}_4/\text{ZnO}$ . The partial current density of  $\text{HCOOH}$  was  $46 \text{ mA cm}^{-2}$  at  $-1.1$  V vs. RHE, which was 2.3-fold and 3.8-fold larger than that of  $\text{Zn}_2\text{SnO}_4$  and  $\text{ZnO}$ , respectively (Fig. 5g). The partial current density of  $\text{H}_2$  and CO on three typical electrocatalysts is shown in Fig. S12.† Accordingly, the half-cell PCE<sup>37</sup> of  $\text{CO}_2$ -to-formate on the  $\text{Zn}_2\text{SnO}_4/\text{ZnO}$  composite was  $\sim 45\%$  over the potential window, which was much higher than that of  $\text{Zn}_2\text{SnO}_4$  and  $\text{ZnO}$  (Fig. 5h). As illustrated by Fig. 5i, a high formate production rate<sup>36</sup> of  $0.17 \mu\text{mol s}^{-1} \text{cm}^{-1}$  was delivered by  $\text{Zn}_2\text{SnO}_4/\text{ZnO}$  at  $-1.1$  V vs. RHE, which was much higher than that of  $\text{ZnO}$  ( $0.08 \mu\text{mol s}^{-1} \text{cm}^{-1}$ ) and  $\text{Zn}_2\text{SnO}_4$  ( $0.12 \mu\text{mol s}^{-1} \text{cm}^{-1}$ ). These data demonstrated the enhanced activity and selectivity of the  $\text{Zn}_2\text{SnO}_4/\text{ZnO}$  composite towards  $\text{CO}_2$ -to-formate conversion.

Inspired by the superior catalytic performance of the composite electrode, the electrochemical active surface area (ECSA) was measured by cyclic voltammetry under various potentials to assess the number of active sites (Fig. S13†). As reported,<sup>40,42,43</sup> ECSA is directly proportional to double-layer capacitance ( $C_{\text{dl}}$ ). As confirmed by Fig. 6a,  $\text{Zn}_2\text{SnO}_4/\text{ZnO}$  exhibited a higher  $C_{\text{dl}}$  ( $0.246 \text{ mF cm}^{-2}$ ) than that of  $\text{Zn}_2\text{SnO}_4$  ( $0.162 \text{ mF cm}^{-2}$ ) or  $\text{ZnO}$  ( $0.196 \text{ mF cm}^{-2}$ ), which indicated more exposed active sites of the composite catalyst. The ECSA of  $\text{Zn}_2\text{SnO}_4/\text{ZnO}$ ,  $\text{ZnO}$  and  $\text{Zn}_2\text{SnO}_4$  was calculated to be  $0.6 \text{ cm}^2$ ,  $0.47 \text{ cm}^2$ , and  $0.39 \text{ cm}^2$ , respectively. However, the ESCA-normalized partial current density of formate for  $\text{Zn}_2\text{SnO}_4/\text{ZnO}$  was  $77 \text{ mA cm}^{-2}$  at  $-1.1$  V vs. RHE, which was 1.5-times and 1.8-times higher than that of  $\text{Zn}_2\text{SnO}_4$  and  $\text{ZnO}$  (Fig. 6b), which demonstrated the enhanced intrinsic catalytic activity of active sites in the  $\text{Zn}_2\text{SnO}_4/\text{ZnO}$  composite. The enhanced ECSA-normalized total current density also confirmed the improvement of catalytic activity of  $\text{Zn}_2\text{SnO}_4/\text{ZnO}$  (Fig. S14†). Electrochemical impedance spectroscopy of three typical catalysts were also measured for the study of charge-transfer kinetics (Fig. 6c).  $\text{Zn}_2\text{SnO}_4/\text{ZnO}$  possessed the fastest electrode kinetics, as evidenced by the smallest charge transfer resistance ( $R_{\text{ct}}$ ) derived from Nyquist plots.<sup>44-46</sup> A chronoamperometric ( $i-t$ ) test at  $-1.0$  V (vs. RHE) was conducted to investigate the electrochemical durability of  $\text{Zn}_2\text{SnO}_4/\text{ZnO}$ . As evidenced by Fig. 6d,  $\text{Zn}_2\text{SnO}_4/\text{ZnO}$  could exhibit an increase in total current density during the first hour of testing, which was attributed to activation of the catalyst. Afterwards, a stable total current density of  $-125 \text{ mA cm}^{-2}$  was maintained over 11 h. The  $\text{FE}_{\text{HCOOH}}$  of  $\text{Zn}_2\text{SnO}_4/\text{ZnO}$  was >80% over the whole period of stability testing, thereby indicating the excellent electrochemical stability of  $\text{Zn}_2\text{SnO}_4/\text{ZnO}$  for  $\text{CO}_2$ -to-formate conversion. Accordingly, the greater number of exposed active sites, excellent ability for electron transfer and optimized



**Fig. 5** (a) LSV curves of  $\text{Zn}_2\text{SnO}_4/\text{ZnO}$ ,  $\text{Zn}_2\text{SnO}_4$  and  $\text{ZnO}$  in 0.5 M  $\text{KHCO}_3$  saturated with  $\text{CO}_2$ . (b)  $i$ - $t$  curves of  $\text{Zn}_2\text{SnO}_4/\text{ZnO}$  at various potentials. FE towards  $\text{H}_2$ ,  $\text{CO}$  and  $\text{HCOOH}$  of (c) prepared  $\text{ZnO}$ , (d)  $\text{Zn}_2\text{SnO}_4$  and (e)  $\text{Zn}_2\text{SnO}_4/\text{ZnO}$ . (f)  $\text{FE}_{\text{HCOOH}}$  of prepared  $\text{ZnO}$ ,  $\text{Zn}_2\text{SnO}_4$  and  $\text{Zn}_2\text{SnO}_4/\text{ZnO}$ . (g)  $\text{HCOOH}$  partial current density of prepared  $\text{ZnO}$ ,  $\text{Zn}_2\text{SnO}_4$  and  $\text{Zn}_2\text{SnO}_4/\text{ZnO}$ . (h) Half-cell PCE for  $\text{CO}_2$ -to-formate conversion for  $\text{Zn}_2\text{SnO}_4/\text{ZnO}$ , prepared  $\text{ZnO}$  and  $\text{Zn}_2\text{SnO}_4$ , respectively. (i) Formate production rate at different voltages for  $\text{Zn}_2\text{SnO}_4/\text{ZnO}$ , prepared  $\text{ZnO}$  and  $\text{Zn}_2\text{SnO}_4$ .



**Fig. 6** (a)  $C_{dl}$  of  $\text{Zn}_2\text{SnO}_4/\text{ZnO}$ ,  $\text{Zn}_2\text{SnO}_4$  and  $\text{ZnO}$ . (b) ECSA-normalized formate partial current density of  $\text{Zn}_2\text{SnO}_4/\text{ZnO}$ ,  $\text{Zn}_2\text{SnO}_4$  and  $\text{ZnO}$ . (c) Nyquist plots of  $\text{Zn}_2\text{SnO}_4/\text{ZnO}$ ,  $\text{Zn}_2\text{SnO}_4$  and  $\text{ZnO}$ . (d) Stability test on the  $\text{Zn}_2\text{SnO}_4/\text{ZnO}$  electrode at  $-1.0$  V (vs. RHE).

surface electronic structure contributed synergistically to the enhanced activity and selectivity of the  $\text{Zn}_2\text{SnO}_4/\text{ZnO}$  composite for electroreduction of  $\text{CO}_2$  to  $\text{HCOO}^-$ .

## Conclusions

A novel  $\text{Zn}_2\text{SnO}_4/\text{ZnO}$  heterostructure nanocomposite catalyst was synthesized *via* a simple one-step hydrothermal method and applied for  $\text{CO}_2$  electroreduction in 0.5 M  $\text{KHCO}_3$  solution. We report, for the first time, that this  $\text{Zn}_2\text{SnO}_4/\text{ZnO}$  hybrid material was employed for electrochemical  $\text{CO}_2$ -to-formate conversion. Advanced characterization involving XPS and X-ray adsorption spectroscopy demonstrated the charge redistribution of  $\text{Zn}_2\text{SnO}_4/\text{ZnO}$  driven by intimate interfacial interaction. The resultant  $\text{Zn}_2\text{SnO}_4/\text{ZnO}$  composite catalyst exhibited significantly enhanced selectivity and activity for  $\text{CO}_2\text{RR}$  to formate compared with that of constituent  $\text{ZnO}$  and  $\text{Zn}_2\text{SnO}_4$ . A remarkable  $\text{FE}_{\text{HCOOH}}$  of up to 87% at  $-1.0$  V *vs.* RHE was

achieved, surpassing the maximum  $FE_{HCOOH}$  of  $ZnO$  (38%) and  $Zn_2SnO_4$  (50%) significantly. The greatly enhanced performance for electrochemical  $CO_2$  reduction to formate was due to the optimized electronic structure, higher electrochemically active surface area and the presence of oxygen vacancies on the surface. Our study may provide new insights for the design of electrocatalysts with high selectivity and activity for  $CO_2RR$  by a synergistic effect of the constructed nanocomposite.

## Conflicts of interest

There are no conflicts to declare.

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