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# Highly efficient electrochemical $CO_2$ reduction over crystalline-amorphous $In_2O_3-CeO_x$ heterostructures†

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The electrochemical reduction reaction of  $CO_2$  ( $CO_2RR$ ) to fuels and chemicals is a promising approach to consume greenhouse gases and mitigate the dependence on fossil fuels. Herein, we synthesized an effective crystalline–amorphous  $In_2O_3$ – $CeO_x$  heterostructure, which exhibited high catalytic performance for  $CO_2$ -to-formate conversion. The maximum faradaic efficiency (FE) of 94.8% was achieved, and above 90% FE can be maintained in a wide potential range from -0.8 to -1.2 V vs. RHE. Detailed studies showed that  $In_2O_3$  functioned as the active site for  $CO_2$  activation and formate formation, and the amorphous  $CeO_x$  was beneficial for the electron transfer, leading to the electronic structure reconfiguration of  $In_2O_3$ . Hence, the  $In_2O_3$ – $CeO_x$  heterostructure enhanced the adsorption of \*OCHO intermediates and lowered the energy barrier forming \*HCOOH from \*OCHO.

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#### Introduction

The electrochemical reduction reaction of CO2 (CO2RR) into value-added chemicals and fuels is a promising approach to consume excess industrial CO2 emissions and address the current ongoing consumption of non-renewable fossil fuels. 1-4 Nevertheless, there are still problems restricting the practical application of the CO<sub>2</sub>RR. For example, CO<sub>2</sub> gas molecules are thermodynamically stable, and the complexity of the reaction pathway as well as the competitive hydrogen evolution reaction (HER) leads to diverse products and low selectivity. Considering the cost of electricity and the product's market price, the twoelectron transfer products formate and CO are the most promising target products among the numerous CO2 reduction products.5 Formate is one of the fundamental starting materials for industrial production, which is widely used in the fields of pesticides, dyes, medicine, rubber and tanning industries.<sup>6</sup> As such, efficient catalysts need to be developed to lower the energy barrier and improve the selectivity for converting CO<sub>2</sub> to formate.

The p-block metals such as In, Bi, Pb, and Sn are efficient catalysts for  $\rm CO_2$  electroreduction due to their high overpotential for the HER.  $^{7-10}$  Among them, low-toxicity and environmentally friendly In-based materials show high selectivity to formate.  $^{11}$ 

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Various strategies on In-based catalysts have been proposed such as morphology design,  $^{12}$  defect engineering,  $^{13}$  doping,  $^{14}$  and alloying  $^{15}$  to reinforce the catalytic activities. Although these strategies are ingenious in design, they still suffer from cumbersome synthetic procedures, and the electrochemical performance still needs to be further improved. As such, the development of novel In-based catalysts is promising for electroreduction of  $CO_2$  to formate.

Constructing heterostructures is an effective strategy to enhance the electrocatalytic performance due to their efficient charge transfer at the interface and the sufficiently exposed catalytically active sites. 16-18 In particular, heterostructures can direct high selectivity toward a specific product in complicated CO2RR reaction routes via adjusting the binding strength with key intermediates. 19,20 CeO2-based materials possess unique transformation characteristics between Ce3+ and Ce4+ states, which are beneficial for the gain and loss of electrons, 21 and have been proved to significantly strengthen the adsorption and promote the activation of CO2 molecules. These properties make CeO2 suitable for constructing heterostructures to enhance the CO2 conversion process. For example, Bao et al. 22 have demonstrated that the CO<sub>2</sub>RR can be significantly improved by the interface of Au-CeO<sub>x</sub> heterostructures. Gong et al. 23 have revealed that high Ce3+ concentration is beneficial for CO<sub>2</sub> activation. Notably, in comparison with their crystalline-crystalline counterparts, crystalline-amorphous heterostructures can inherit the merits of amorphous structures, such as abundant active sites and defects, high flexibility, and better corrosion resistance. 24,25 Therefore, rational design of crystalline-amorphous heterostructures is an effective method to achieve the purpose of improving CO<sub>2</sub>RR performance.

Herein, crystalline-amorphous In<sub>2</sub>O<sub>3</sub>-CeO<sub>x</sub> heterostructures were fabricated for the first time and were used as an electrocatalyst for the CO2RR. It was discovered that the maximum faradaic efficiency (FE) can reach 94.8% at −0.9 V vs. RHE over In<sub>2</sub>O<sub>3</sub>-CeO<sub>x</sub>, which was obviously more efficient than those of a pure In<sub>2</sub>O<sub>3</sub> catalyst and a crystalline-crystalline In<sub>2</sub>O<sub>3</sub>-CeO<sub>2</sub> heterostructure. The improved performance of the In<sub>2</sub>O<sub>3</sub>-CeO<sub>x</sub> catalyst was attributed to the electronic reconfiguration of indium by strengthened electron transfer between In2O3 and amorphous CeO<sub>x</sub>, which significantly enhanced the adsorption of \*OCHO intermediates and lowered the energy barrier of \*OCHO → \*HCOOH, leading to the high activity and selectivity for the CO<sub>2</sub>RR to formate.

## Results and discussion

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The In<sub>2</sub>O<sub>3</sub>-CeO<sub>r</sub> catalyst was synthesized via two steps (Fig. S1a†). Firstly, an aqueous solution containing indium nitrate, sodium carbonate and as-prepared CeOx was stirred to form an In(OH)3-CeOx precipitate for one hour at room temperature. Secondly, the precursor In(OH)3-CeOx was annealed under an Ar/H<sub>2</sub> flow for one hour to obtain the In<sub>2</sub>O<sub>3</sub>-CeO<sub>x</sub> catalyst. The structures of the samples (e.g., In<sub>2</sub>O<sub>3</sub>-CeO<sub>x</sub>, In<sub>2</sub>O<sub>3</sub>-CeO<sub>2</sub>, the individual CeO<sub>x</sub>, CeO<sub>2</sub> and In<sub>2</sub>O<sub>3</sub>) were determined using X-ray diffraction (XRD) patterns. As shown in Fig. 1a, no obvious peak was observed for CeOx, suggesting that the amorphous structure was successfully achieved. In addition, no obvious peak of In2O3 was observed in the In2O3-CeO<sub>r</sub> sample, which was caused by the small particle size and uniform dispersion of In<sub>2</sub>O<sub>3</sub>. In contrast, CeO<sub>2</sub> displayed the characteristic peaks of the crystal structure, which were con-

sistent with those reported in the literature (Fig. 1b).<sup>26</sup> The (a) CeO 60 40 50 60 2 Theta / degree n<sub>2</sub>O<sub>3</sub> PDF#06-0416 2 Theta / degree (h) (j)

Fig. 1 (a) XRD patterns of  $CeO_x$  and  $In_2O_3-CeO_{x_r}$  (b) XRD patterns of  $CeO_2$  and  $In_2O_3-CeO_2$ , (c and d) HR-TEM image of  $In_2O_3-CeO_x$  and (e and f) HR-TEM image of In<sub>2</sub>O<sub>3</sub>-CeO<sub>2</sub>. (g-j) The corresponding EDX elemental mapping of In2O3CeOx.

peaks of In<sub>2</sub>O<sub>3</sub>-CeO<sub>2</sub> matched well with the standard patterns of CeO<sub>2</sub> and In<sub>2</sub>O<sub>3</sub>, as shown in Fig. 1b. The high-resolution transmission electron microscopy (HR-TEM) images showed the crystalline-amorphous heterostructure interface of In<sub>2</sub>O<sub>3</sub>-CeO<sub>x</sub> and crystalline-crystalline heterostructure interface of In<sub>2</sub>O<sub>3</sub>-CeO<sub>2</sub> (Fig. 1c-f). As shown in Fig. 1d, the lattice fringe of In<sub>2</sub>O<sub>3</sub>-CeO<sub>x</sub> could be assigned to the (222) plane of In<sub>2</sub>O<sub>3</sub> while the amorphous CeO<sub>x</sub> did not show any lattice stripes. In contrast, the HR-TEM image of In2O3-CeO2 clearly presented the lattice fringes for the (222) facet of In<sub>2</sub>O<sub>3</sub> and (111) facet of CeO2 (Fig. 1f). Furthermore, energy dispersive X-ray spectroscopy (EDX) elemental mapping of the samples showed that In, Ce, and O were evenly distributed (Fig. 1g-j and S2†), confirming the successful preparation of In<sub>2</sub>O<sub>3</sub>-CeO<sub>x</sub> and In<sub>2</sub>O<sub>3</sub>-CeO<sub>2</sub> heterostructures.

X-ray photoelectron spectroscopy (XPS) was utilized to investigate the electronic properties and chemical compositions of the samples. The Ce 3d XPS spectra of  $CeO_x$  showed the presence of both Ce<sup>4+</sup> and Ce<sup>3+</sup> peaks (Fig. 2a), where Ce<sup>3+</sup> included one pair of peaks (V and V'), whilst Ce4+ had two pairs of peaks  $(U_1, U_2, U_1, and U_2)$ . Notably, the proportion of  $Ce^{3+}$  in  $In_2O_3$ - $CeO_x$  was increased to 48.3% (Fig. 2b) compared to the individual CeO<sub>x</sub> (43.2%). In contrast, the proportion of Ce<sup>3+</sup> in In<sub>2</sub>O<sub>3</sub>-CeO<sub>2</sub> showed no obvious variation compared to that in CeO<sub>2</sub> (Fig. S3a and b†). Additionally, the In 3d spectra of In<sub>2</sub>O<sub>3</sub> showed two peaks at 451.7 (In 3d<sub>3/2</sub>) and 444.2 eV (In  $3d_{5/2}$ ), while the binding energy of In 3d in  $In_2O_3$ -CeO<sub>x</sub> shifted positively about 1 eV compared to that of In<sub>2</sub>O<sub>3</sub> (Fig. 2c). The results demonstrated the strong interaction between In2O3 and CeO<sub>x</sub>, and electrons transferred from the crystalline In<sub>2</sub>O<sub>3</sub> to amorphous CeOx, which led to an increase in the proportion of  $Ce^{3+}$  in  $In_2O_3$ - $CeO_x$ . Moreover, the linear sweep voltammetry (LSV) curves of In2O3 showed an obvious reduction peak at

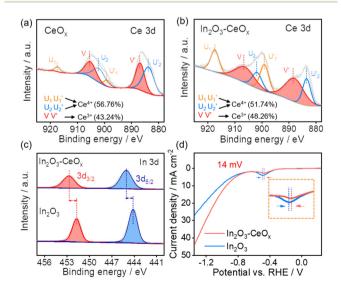


Fig. 2 Ce 3d XPS spectra of (a) CeO<sub>x</sub> and (b) In<sub>2</sub>O<sub>3</sub>-CeO<sub>x</sub>; (c) In 3d XPS spectra of  $ln_2O_3$ -CeO<sub>x</sub> and  $ln_2O_3$ ; and (d) LSVs of  $ln_2O_3$  and  $ln_2O_3$ - $CeO_x$  in  $CO_2$ -saturated 0.5 M KHCO<sub>3</sub> at a scan rate of 50 mV s<sup>-1</sup>.

-0.487 V (vs. RHE), corresponding to a typical In<sup>3+</sup>/In<sup>0</sup> reduction peak (Fig. S4†).<sup>27</sup>

It should be noted that the reduction peak potential of  $In_2O_3$ – $CeO_x$  positively shifted by 14 mV (appearing at -0.473 V) (Fig. 2d). The lower reduction potential of  $In_2O_3$ – $CeO_x$  meant an enhanced electrochemical redox activity. <sup>28</sup> In contrast, no obvious change in the reduction peak potential was detected for  $In_2O_3$ – $CeO_2$  compared to that of  $In_2O_3$  (Fig. S3c†). This result was consistent with the XPS data, revealing that the crystalline–amorphous heterostructure of  $In_2O_3$ – $CeO_x$  led to stronger interactions between its individual components.

The electrocatalytic  $CO_2RR$  performances of  $In_2O_3$ ,  $In_2O_3$ – $CeO_x$ , and  $In_2O_3$ – $CeO_2$  were tested in a three-electrode system, with  $CO_2$  saturated 0.1 M KHCO $_3$  as an electrolyte. Linear sweep voltammetry (LSV) curves were obtained at a scan rate of 50 mV s $^{-1}$  between -1.38 V and -0.62 V ( $\nu s$ . RHE, all potentials used were  $\nu s$ . RHE unless otherwise stated). As depicted by the linear sweep voltammetry (LSV) curves of all catalysts (Fig. 3a and S5 $^{\dagger}$ ), significantly higher current density was observed in  $CO_2$  than that under an Ar atmosphere, indicating that the  $CO_2$  reduction reaction occurred over these catalysts. Meanwhile, the current density of  $In_2O_3$ – $CeO_x$  was larger than those of  $In_2O_3$ – $CeO_2$  and  $In_2O_3$  in a  $CO_2$ -saturated electrolyte, indicating that a crystalline–amorphous  $In_2O_3$ – $CeO_x$  heterostructure shows the best  $CO_2RR$  performance.

To further analyze the electroreduction products, controlled potential electrolysis of  $CO_2$  was performed at a constant working potential ranging from -0.6 V to -1.3 V. The gaseous and liquid products were quantified by gas chromatography (GC) and nuclear magnetic resonance (NMR) spectroscopy, respectively. For  $In_2O_3$ ,  $In_2O_3$ – $CeO_2$  and  $In_2O_3$ – $CeO_x$  catalysts, CO and  $H_2$  were detected as gas products, and formate was the

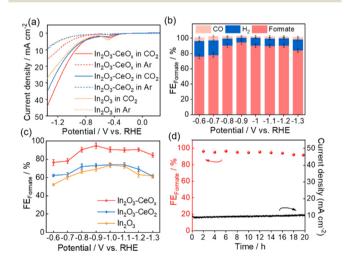


Fig. 3 CO $_2$  electroreduction in a 0.5 M KHCO $_3$  electrolyte. (a) LSV curves of  $In_2O_3-CeO_x$ ,  $In_2O_3-CeO_2$  and  $In_2O_3$  electrodes in a CO $_2$ -saturated electrolyte. (b) The FE $_{formate}$ , FE $_{CO}$  and FE $_{H_2}$  of  $In_2O_3-CeO_x$  at different applied potentials, respectively. (c) FE $_{formate}$  of  $In_2O_3-CeO_x$ ,  $In_2O_3-CeO_2$  and  $In_2O_3$  at different applied potentials, respectively. (d) Long-term stability of the CO $_2$  electroreduction for  $In_2O_3-CeO_x$  at -0.9 V (vs. RHE).

unique liquid product (Fig. S6†). The formate faradaic efficiency (FE<sub>formate</sub>) of the three catalysts all exhibited a volcanic-like pattern over the range of applied operating potentials, among which, the In2O3-CeOx electrode exhibited higher selectivity toward formate against H2 and CO (Fig. 3b and c). More remarkably, the  $FE_{formate}$  on the  $In_2O_3$ - $CeO_x$  electrode remained above 90% over a wide electrochemical window from -0.8 V to −1.2 V. The maximum FE<sub>formate</sub> reached 94.8% with a current density of 7 mA cm $^{-2}$  at -0.9 V (Fig. 3c). By comparison, the maximum FE<sub>formate</sub> for In<sub>2</sub>O<sub>3</sub>-CeO<sub>2</sub> and In<sub>2</sub>O<sub>3</sub> electrodes was only 74.2% and 73.6%, respectively, under -1.0 V (Fig. S7a and b†). The optimal electrolysis potential of In<sub>2</sub>O<sub>3</sub>- $CeO_x$  was more positive than that of  $In_2O_3$  and  $In_2O_3$ - $CeO_2$ , which suggested that lower electrical energy was required to cross the energy barrier and realize the CO2RR by the In2O3-CeO<sub>x</sub> catalyst. Notably, H<sub>2</sub> was the only product of the individual  $CeO_x$  and  $CeO_2$  (Fig. S7c and d†), indicating that the amorphous and crystalline ceria contributed to the formate formation via functions rather than being the catalyst.

The stability of In<sub>2</sub>O<sub>3</sub>–CeO<sub>x</sub> was tested by continuous electrolysis at –0.9 V. As shown in Fig. 3d, no evident decay of current density and FE<sub>formate</sub> was observed after 20 h-electrolysis, demonstrating the good stability of the prepared In<sub>2</sub>O<sub>3</sub>–CeO<sub>x</sub> electrode. Moreover, the LSV curves before and after long-term test showed no obvious difference (Fig. S8†), which further manifested the good stability of In<sub>2</sub>O<sub>3</sub>–CeO<sub>x</sub>. After the test, the element mapping of In<sub>2</sub>O<sub>3</sub>–CeO<sub>x</sub> showed that In, Ce, and O were uniformly distributed (Fig. S9†). In addition, the HRTEM image of In<sub>2</sub>O<sub>3</sub>–CeO<sub>x</sub> after electrolysis still showed the amorphous morphology of CeO<sub>x</sub> and the (222) plane of In<sub>2</sub>O<sub>3</sub> (Fig. S9a and b†), indicating that the crystalline–amorphous heterostructure of In<sub>2</sub>O<sub>3</sub>–CeO<sub>x</sub> can be retained during the electrolytic process.

To gain a deeper understanding of the kinetics of CO<sub>2</sub> electroreduction, we fitted the overpotentials of the three catalysts as a function of the bias current density for formate production to obtain the corresponding Tafel slopes (Fig. 4a). In<sub>2</sub>O<sub>3</sub>-CeO<sub>x</sub> presented a smaller calculated Tafel slope (176 mV  $dec^{-1}$ ) compared to  $In_2O_3$ - $CeO_2$  (186 mV  $dec^{-1}$ ) and pure  $In_2O_3$  (375 mV dec<sup>-1</sup>). The smallest Tafel slope of  $In_2O_3$ -CeO<sub>x</sub> suggested the largest increment in the CO<sub>2</sub> reduction rate with the increasing overpotential. The electron transfer properties were further investigated by an electrochemical impedance spectroscopy (EIS) test. As shown in Fig. 4b, In<sub>2</sub>O<sub>3</sub>-CeO<sub>x</sub> showed smaller charge transfer resistance ( $R_{ct}$ ) compared to In<sub>2</sub>O<sub>3</sub>-CeO<sub>2</sub> and In<sub>2</sub>O<sub>3</sub>. The results suggested that the crystalline-amorphous heterostructure rendered faster charge transfer than the bare In2O3 and crystalline-crystalline heterostructure, and the interaction of electrochemically active In2O3 with the amorphous CeO<sub>x</sub> led to a more efficient electron transfer. The electrochemically active surface area (ECSA) was evaluated by the electrochemical double layer capacitance  $(C_{dl})$ due to their positive proportion relationship (Fig. 4c).<sup>2,29,30</sup> The ECSA of  $In_2O_3$ - $CeO_x$  (13.75 cm<sup>-2</sup>) was higher than those of In<sub>2</sub>O<sub>3</sub>-CeO<sub>2</sub> (11.50 cm<sup>-2</sup>) and In<sub>2</sub>O<sub>3</sub> (9.50 cm<sup>-2</sup>), which can promote the electrocatalytic performance. In addition, the

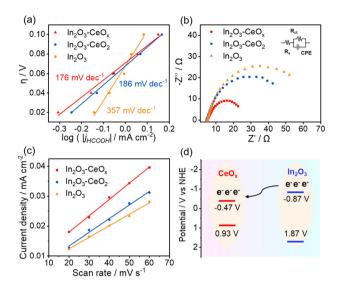


Fig. 4 Advantages of In<sub>2</sub>O<sub>3</sub>-CeO<sub>x</sub> for CO<sub>2</sub> reduction. (a) Tafel plots, (b) Nyquist plots (inset: equivalent circuit), (c) linear fitting of double-layer capacitive currents versus scan rates to estimate the ECSA of In<sub>2</sub>O<sub>3</sub>-CeO<sub>x</sub>, In<sub>2</sub>O<sub>3</sub>-CeO<sub>2</sub> and In<sub>2</sub>O<sub>3</sub>, and (d) schematic illustration of the charge transfer in In<sub>2</sub>O<sub>2</sub>-CeO<sub>4</sub>

partial current density of formate was normalized by the ECSA (Fig. S11†).<sup>2</sup> Similar to the geometric current density, the normalized current density of In<sub>2</sub>O<sub>3</sub>-CeO<sub>x</sub> was the highest among the three samples. The rough surface of the CeO<sub>x</sub> substrate promoted the adsorption and dispersion of In<sub>2</sub>O<sub>3</sub>, thereby increasing the active surface area. Furthermore, to verify the phenomenon of electron transfer between In<sub>2</sub>O<sub>3</sub> and CeO<sub>x</sub> in In<sub>2</sub>O<sub>3</sub>-CeO<sub>x</sub>, we performed Mott-Schottky and valence band XPS experiments (Fig. S12†). As shown in Fig. 4d, the flat band potentials of In<sub>2</sub>O<sub>3</sub> and CeO<sub>x</sub> were located at -0.87 V and -0.47 V (vs. NHE), respectively. Such a band alignment can effectively facilitate the interfacial electrons transferring from the key component In<sub>2</sub>O<sub>3</sub> to CeO<sub>x</sub>. However, the flat band and valence band potentials of CeO<sub>2</sub> and In<sub>2</sub>O<sub>3</sub> were not significantly different (Fig. S13†), and thus electron transfer hardly occurred between CeO2 and In2O3.

Density functional theory (DFT) calculations were carried out to shed light on the origin of the enhanced activity of  $In_2O_3$ -CeO<sub>x</sub> for the CO<sub>2</sub>RR (Fig. S14-S16†). The charge density difference and charge displacement curves of In2O3-CeOx and In<sub>2</sub>O<sub>3</sub>-CeO<sub>2</sub> were obtained to study the transfer of electrons.31-33 As shown in Fig. 5a, the positive and negative signals of the charge displacement curve represented electron accumulation and depletion, respectively. The In<sub>2</sub>O<sub>3</sub>-CeO<sub>x</sub> heterostructure displayed a significant charge rearrangement around the crystalline-amorphous heterostructure interface, and electron transfer took place from In<sub>2</sub>O<sub>3</sub> to CeO<sub>x</sub>, which was in good agreement with the XPS results. Moreover, the reaction pathways for the generation of formate were considered. According to the calculations, the Gibbs free energy for the rate-determining step (RDS) on In<sub>2</sub>O<sub>3</sub>-CeO<sub>x</sub> is lower than that on In<sub>2</sub>O<sub>3</sub>-CeO<sub>2</sub> and In<sub>2</sub>O<sub>3</sub> for the CO<sub>2</sub>-to-formate

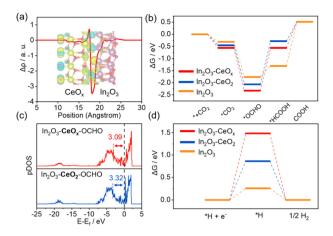


Fig. 5 DFT calculations. (a) Charge density difference and charge displacement curves of In<sub>2</sub>O<sub>3</sub>-CeO<sub>x</sub>; purple, yellow, and red spheres represent In, Ce, and O atoms, respectively. (b) Gibbs free-energy diagrams of CO2-to-formate. (c) In-5p p-DOS of In2O3-CeOx and In2O3-CeO2 after adsorbing \*OCHO. (d) Gibbs free-energy diagrams of the HER.

process (Fig. 5b), suggesting that In<sub>2</sub>O<sub>3</sub>-CeO<sub>x</sub> was thermodynamically more favourable for CO2-to-formate conversion. The adsorption energies of the \*OCHO intermediates on In<sub>2</sub>O<sub>3</sub>-CeO<sub>x</sub> and In<sub>2</sub>O<sub>3</sub>-CeO<sub>2</sub> were further explained by the projected density of states (p-DOS). As shown in Fig. 5c, the centre of the p-band for In<sub>2</sub>O<sub>3</sub>-CeO<sub>x</sub>-\*OCHO was closer to the Fermi level compared with that of In2O3-CeO2-\*OCHO, which verified that the antibonding state filling of the In-5p orbital of In<sub>2</sub>O<sub>3</sub>-CeO<sub>x</sub> is lower than that of In<sub>2</sub>O<sub>3</sub>-CeO<sub>2</sub>, thereby enhancing the adsorption strength of \*OCHO.14 In addition, the Gibbs free energy for the dominant competitive HER was also explored (Fig. 5d). The Gibbs free energy for generating \*H over In<sub>2</sub>O<sub>3</sub>-CeO<sub>r</sub> was much larger than that for In<sub>2</sub>O<sub>3</sub>-CeO<sub>2</sub> and In<sub>2</sub>O<sub>3</sub>, indicating that the HER was more difficult to occur on In<sub>2</sub>O<sub>3</sub>-CeO<sub>x</sub>. Therefore, the crystalline-amorphous In<sub>2</sub>O<sub>3</sub>- $CeO_x$  heterostructure accelerated the electron transfer, enhanced the adsorption to \*OCHO, lowered the energy barrier for the process from OCHO\* to \*HCOOH, and finally promoted the formation of the formate product. Furthermore, the In<sub>2</sub>O<sub>3</sub>-CeO<sub>x</sub> catalyst significantly suppressed the HER competition reaction compared with In<sub>2</sub>O<sub>3</sub> and In<sub>2</sub>O<sub>3</sub>-CeO<sub>2</sub>.

#### Conclusion

In conclusion, we described a facile strategy to fabricate the crystalline-amorphous In<sub>2</sub>O<sub>3</sub>-CeO<sub>x</sub> heterostructure studied its performance for the CO2RR. The experimental results showed that In<sub>2</sub>O<sub>3</sub>-CeO<sub>x</sub> achieved better catalytic performance than the crystalline-crystalline In<sub>2</sub>O<sub>3</sub>-CeO<sub>2</sub> heterostructure and In<sub>2</sub>O<sub>3</sub> alone. The maximum FE of 94.8% was achieved on the In2O3-CeOx catalyst, and the FE remained above 90% over a wide potential range of -0.8 to -1.2 V vs. RHE. Detailed studies have shown that there was a remarkable electron transfer from In<sub>2</sub>O<sub>3</sub> to amorphous CeO<sub>x</sub> on the In<sub>2</sub>O<sub>3</sub>-

CeO<sub>x</sub> heterostructure compared to the crystalline-crystalline In<sub>2</sub>O<sub>3</sub>-CeO<sub>2</sub> heterostructure, which decreased the interfacial charge transfer resistance. The In<sub>2</sub>O<sub>3</sub>-CeO<sub>x</sub> heterostructure promoted the adsorption for \*OCHO intermediates and thereby the energy barrier of \*OCHO → \*HCOOH was reduced, which led to the high selectivity of the CO<sub>2</sub>RR to formate. We believe that the work may provide an effective strategy for catalysing CO2 conversion.

#### Conflicts of interest

Research Article

There are no conflicts to declare.

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#### Notes and references

- 1 Y. Y. Birdja, E. Pérez-Gallent, M. C. Figueiredo, A. J. Göttle, F. Calle-Vallejo and M. T. M. Koper, Advances and challenges in understanding the electrocatalytic conversion of carbon dioxide to fuels, Nat. Energy, 2019, 4, 732-745.
- 2 C. Chen, X. Sun, X. Yan, Y. Wu, H. Liu, Q. Zhu, B. B. A. Bediako and B. Han, Boosting CO2 electroreduction on N,P-Co-doped carbon aerogels, Angew. Chem., Int. Ed., 2020, 59, 11123-11129.
- 3 W. Guo, X. Tan, J. Bi, L. Xu, D. Yang, C. Chen, Q. Zhu, J. Ma, A. Tayal, J. Ma, Y. Huang, X. Sun, S. Liu and B. Han, Atomic indium catalysts for switching CO<sub>2</sub> electroreduction products from formate to CO, J. Am. Chem. Soc., 2021, 143, 6877-6885.
- 4 Z. Wang, Y. Zhou, C. Xia, W. Guo, B. You and B. Y. Xia, Efficient electroconversion of carbon dioxide to formate by reconstructed amino-functionalized indium-organic framework electrocatalyst, Angew. Chem., Int. Ed., 2021, 60, 19107-19112.
- 5 N. Han, P. Ding, L. He, Y. Li and Y. Li, Promises of main group metal-based nanostructured materials for electrochemical CO2 reduction to formate, Adv. Energy Mater., 2020, 10, 1902338.
- 6 F. Valentini, V. Kozell, C. Petrucci, A. Marrocchi, Y. Gu, D. Gelman and L. Vaccaro, Formic acid, a biomass-derived source of energy and hydrogen for biomass upgrading, Energy Environ. Sci., 2019, 12, 2646-2664.
- 7 W. Guo, S. Liu, X. Tan, R. Wu, X. Yan, C. Chen, Q. Zhu, L. Zheng, J. Ma, J. Zhang, Y. Huang, X. Sun and B. Han, Highly efficient CO<sub>2</sub> electroreduction to methanol through

- atomically dispersed Sn coupled with defective CuO catalysts, Angew. Chem., Int. Ed., 2021, 60, 21979-21987.
- 8 L. Lu, W. Guo, C. Chen, Q. Zhu, J. Ma, H. Wu, D. Yang, G. Yang, X. Sun and B. Han, Synthesis of Sn<sub>4</sub>P<sub>3</sub>/reduced graphene oxide nanocomposites as highly efficient electrocatalysts for CO<sub>2</sub> reduction, Green Chem., 2020, 22, 6804-6808.
- 9 D. Yang, Q. Zhu, X. Sun, C. Chen, W. Guo, G. Yang and B. Han, Electrosynthesis of a defective indium selenide with 3D structure on a substrate for tunable CO2 electroreduction to syngas, Angew. Chem., Int. Ed., 2020, 59, 2354-
- 10 J. E. Pander, M. F. Baruch and A. B. Bocarsly, Probing the mechanism of aqueous CO2 reduction on post-transitionmetal electrodes using ATR-IR spectroelectrochemistry, ACS Catal., 2016, 6, 7824-7833.
- 11 J. Li, M. Zhu and Y.-F. Han, Recent advances in electrochemical CO2 reduction on indium-based catalysts, ChemCatChem, 2021, 13, 514-531.
- 12 Y. Huang, X. Mao, G. Yuan, D. Zhang, B. Pan, J. Deng, Y. Shi, N. Han, C. Li, L. Zhang, L. Wang, L. He, Y. Li and Y. Li, Size-dependent selectivity of electrochemical CO<sub>2</sub> reduction on converted In<sub>2</sub>O<sub>3</sub> nanocrystals, Angew. Chem., Int. Ed., 2021, 60, 15844-15848.
- 13 J. Zhang, R. Yin, Q. Shao, T. Zhu and X. Huang, Oxygen vacancies in amorphous InOx nanoribbons enhance CO2 adsorption and activation for CO2 electroreduction, Angew. Chem., Int. Ed., 2019, 58, 5609-5613.
- 14 Z. Chen, G. Yu, B. Li, X. Zhang, M. Jiao, N. Wang, X. Zhang and L. Liu, In situ carbon encapsulation confined nickeldoped indium oxide nanocrystals for boosting CO2 electroreduction to the industrial level, ACS Catal., 2021, 11, 14596-14604.
- 15 W. Luo, W. Xie, R. Mutschler, E. Oveisi, G. L. De Gregorio, R. Buonsanti and A. Züttel, Selective and stable electroreduction of CO2 to CO at the copper/indium interface, ACS Catal., 2018, 8, 6571-6581.
- 16 M. A. Ahsan, T. He, J. C. Noveron, K. Reuter, A. R. Puente-Santiago and R. Luque, Low-dimensional heterostructures for advanced electrocatalysis: an experimental and computational perspective, Chem. Soc. Rev., 2022, 51, 812-828.
- 17 P. Prabhu, V. Jose and J.-M. Lee, Heterostructured catalysts for electrocatalytic and photocatalytic carbon dioxide reduction, Adv. Funct. Mater., 2020, 30, 1910768.
- 18 A. Vasileff, C. Xu, Y. Jiao, Y. Zheng and S.-Z. Qiao, Surface and interface engineering in copper-based bimetallic materials for selective CO2 electroreduction, Chem, 2018, 4, 1809-1831.
- 19 P.-F. Sui, C. Xu, M.-N. Zhu, S. Liu, Q. Liu and J.-L. Luo, Interface-induced electrocatalytic enhancement of CO<sub>2</sub>-toformate conversion on heterostructured bismuth-based catalysts, Small, 2022, 18, 2105682.
- 20 Z. Zhang, F. Ahmad, W. Zhao, W. Yan, W. Zhang, H. Huang, C. Ma and J. Zeng, Enhanced electrocatalytic reduction of CO<sub>2</sub> via chemical coupling between indium

- oxide and reduced graphene oxide, Nano Lett., 2019, 19, 4029-4034.
- 21 J. Wang, X. Xiao, Y. Liu, K. Pan, H. Pang and S. Wei, The application of CeO2-based materials in electrocatalysis, J. Mater. Chem. A, 2019, 7, 17675-17702.
- 22 D. Gao, Y. Zhang, Z. Zhou, F. Cai, X. Zhao, W. Huang, Y. Li, J. Zhu, P. Liu, F. Yang, G. Wang and X. Bao, Enhancing CO<sub>2</sub> electroreduction with the metal-oxide interface, I. Am. Chem. Soc., 2017, 139, 5652-5655.
- 23 H. Dong, L. Zhang, L. Li, W. Deng, C. Hu, Z.-J. Zhao and J. Gong, Abundant Ce<sup>3+</sup> ions in Au-CeO<sub>x</sub> nanosheets to enhance CO<sub>2</sub> electroreduction performance, Small, 2019, **15**, 1900289.
- 24 S. Shen, Z. Wang, Z. Lin, K. Song, Q. Zhang, F. Meng, L. Gu and W. Zhong, Crystalline-amorphous interfaces coupling of CoSe<sub>2</sub>/CoP with optimized d-band center and boosted electrocatalytic hydrogen evolution, Adv. Mater., 2022, 34, 2110631.
- 25 M. Yang, M. Zhao, J. Yuan, J. Luo, J. Zhang, Z. Lu, D. Chen, X. Fu, L. Wang and C. Liu, Oxygen vacancies and interface engineering on amorphous/crystalline CrOx-Ni3N heterostructures toward high-durability and kinetically accelerated water splitting, Small, 2022, 18, 2106554.
- 26 Y. X. Duan, Y. T. Zhou, Z. Yu, D. X. Liu, Z. Wen, J. M. Yan and O. Jiang, Boosting Production of HCOOH from CO2 Electroreduction via Bi/CeOx, Angew. Chem., Int. Ed., 2021, 60, 8798-8802.
- 27 Z. M. Detweiler, J. L. White, S. L. Bernasek and A. B. Bocarsly, Anodized indium metal electrodes for

- enhanced carbon dioxide reduction in aqueous electrolyte, Langmuir, 2014, 30, 7593-7600.
- 28 F. Yang, X. Bao, P. Li, X. Wang, G. Cheng, S. Chen and W. Luo, Boosting hydrogen oxidation activity of Ni in alkamedia through oxygen-vacancy-Rich CeO<sub>2</sub>/Ni heterostructures, Angew. Chem., Int. Ed., 2019, 58, 14179-14183.
- 29 Y. Wang, W. Zhou, R. Jia, Y. Yu and B. Zhang, Unveiling the activity origin of a copper-based electrocatalyst for selective nitrate reduction to ammonia, Angew. Chem., Int. Ed., 2020, **59**, 5350-5354.
- 30 C. Zhang, Y. Huang, Y. Yu, J. Zhang, S. Zhuo and B. Zhang, Sub-1.1 nm ultrathin porous CoP nanosheets with dominant reactive {200} facets: a high mass activity and efficient electrocatalyst for the hydrogen evolution reaction, Chem. Sci., 2017, 8, 2769-2775.
- 31 G. Ciancaleoni, F. Nunzi and L. Belpassi, Charge displacement analysis-A tool to theoretically characterize the charge transfer contribution of halogen bonds, Molecules, 2020, 25, 300-316.
- 32 Y. Zhou, Y. Yao, R. Zhao, X. Wang, Z. Fu, D. Wang, H. Wang, L. Zhao, W. Ni, Z. Yang and Y. M. Yan, Stabilization of Cu<sup>+</sup> via strong electronic interaction for selective and stable CO2 electroreduction, Angew. Chem., Int. Ed., 2022, 61, e202205832.
- 33 D. Sorbelli, E. Rossi, R. W. A. Havenith, J. Klein, L. Belpassi and P. Belanzoni, Gold-aluminyl and gold-diarylboryl complexes: bonding and reactivity with carbon dioxide, Inorg. Chem., 2022, 61, 7327-7337.