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 Cite this: *Inorg. Chem. Front.*, 2022, **9**, 5926

Highly efficient electrochemical CO₂ reduction over crystalline–amorphous In₂O₃–CeO_x heterostructures†

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The electrochemical reduction reaction of CO₂ (CO₂RR) 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 In₂O₃–CeO_x heterostructure, which exhibited high catalytic performance for CO₂-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 In₂O₃ functioned as the active site for CO₂ activation and formate formation, and the amorphous CeO_x was beneficial for the electron transfer, leading to the electronic structure reconfiguration of In₂O₃. Hence, the In₂O₃–CeO_x heterostructure enhanced the adsorption of *OCHO intermediates and lowered the energy barrier forming *HCOOH from *OCHO.

 Received 29th July 2022,
 Accepted 29th September 2022

DOI: 10.1039/d2qi01646j

rsc.li/frontiers-inorganic

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 CO₂RR. For example, CO₂ 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 two-electron 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.⁶ As such, efficient catalysts need to be developed to lower the energy barrier and improve the selectivity for converting CO₂ to formate.

The p-block metals such as In, Bi, Pb, and Sn are efficient catalysts for CO₂ 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

Various strategies on In-based catalysts have been proposed such as morphology design,¹² defect engineering,¹³ doping,¹⁴ and alloying¹⁵ 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 CO₂ 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 CO₂RR can be significantly improved by the interface of Au–CeO_x heterostructures. Gong *et al.*²³ have revealed that high Ce³⁺ concentration is beneficial for CO₂ 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 CO₂RR performance.

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† Electronic supplementary information (ESI) available. See DOI: <https://doi.org/10.1039/d2qi01646j>

Herein, crystalline–amorphous $\text{In}_2\text{O}_3\text{--CeO}_x$ heterostructures were fabricated for the first time and were used as an electro-catalyst for the CO_2RR . It was discovered that the maximum faradaic efficiency (FE) can reach 94.8% at -0.9 V vs. RHE over $\text{In}_2\text{O}_3\text{--CeO}_x$, which was obviously more efficient than those of a pure In_2O_3 catalyst and a crystalline–crystalline $\text{In}_2\text{O}_3\text{--CeO}_2$ heterostructure. The improved performance of the $\text{In}_2\text{O}_3\text{--CeO}_x$ catalyst was attributed to the electronic reconfiguration of indium by strengthened electron transfer between In_2O_3 and amorphous CeO_x , which significantly enhanced the adsorption of $^*\text{OCHO}$ intermediates and lowered the energy barrier of $^*\text{OCHO} \rightarrow ^*\text{HCOOH}$, leading to the high activity and selectivity for the CO_2RR to formate.

Results and discussion

The $\text{In}_2\text{O}_3\text{--CeO}_x$ catalyst was synthesized *via* two steps (Fig. S1a†). Firstly, an aqueous solution containing indium nitrate, sodium carbonate and as-prepared CeO_x was stirred to form an $\text{In}(\text{OH})_3\text{--CeO}_x$ precipitate for one hour at room temperature. Secondly, the precursor $\text{In}(\text{OH})_3\text{--CeO}_x$ was annealed under an Ar/H_2 flow for one hour to obtain the $\text{In}_2\text{O}_3\text{--CeO}_x$ catalyst. The structures of the samples (*e.g.*, $\text{In}_2\text{O}_3\text{--CeO}_x$, $\text{In}_2\text{O}_3\text{--CeO}_2$, the individual CeO_x , CeO_2 and In_2O_3) were determined using X-ray diffraction (XRD) patterns. As shown in Fig. 1a, no obvious peak was observed for CeO_x , suggesting that the amorphous structure was successfully achieved. In addition, no obvious peak of In_2O_3 was observed in the $\text{In}_2\text{O}_3\text{--CeO}_x$ sample, which was caused by the small particle size and uniform dispersion of In_2O_3 . In contrast, CeO_2 displayed the characteristic peaks of the crystal structure, which were consistent with those reported in the literature (Fig. 1b).²⁶ The

peaks of $\text{In}_2\text{O}_3\text{--CeO}_2$ matched well with the standard patterns of CeO_2 and In_2O_3 , as shown in Fig. 1b. The high-resolution transmission electron microscopy (HR-TEM) images showed the crystalline–amorphous heterostructure interface of $\text{In}_2\text{O}_3\text{--CeO}_x$ and crystalline–crystalline heterostructure interface of $\text{In}_2\text{O}_3\text{--CeO}_2$ (Fig. 1c–f). As shown in Fig. 1d, the lattice fringe of $\text{In}_2\text{O}_3\text{--CeO}_x$ could be assigned to the (222) plane of In_2O_3 while the amorphous CeO_x did not show any lattice stripes. In contrast, the HR-TEM image of $\text{In}_2\text{O}_3\text{--CeO}_2$ clearly presented the lattice fringes for the (222) facet of In_2O_3 and (111) facet of CeO_2 (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 $\text{In}_2\text{O}_3\text{--CeO}_x$ and $\text{In}_2\text{O}_3\text{--CeO}_2$ 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^{4+} and Ce^{3+} peaks (Fig. 2a), where Ce^{3+} included one pair of peaks (V and V'), whilst Ce^{4+} had two pairs of peaks (U_1, U_2, U'_1 , and U'_2). Notably, the proportion of Ce^{3+} in $\text{In}_2\text{O}_3\text{--CeO}_x$ was increased to 48.3% (Fig. 2b) compared to the individual CeO_x (43.2%). In contrast, the proportion of Ce^{3+} in $\text{In}_2\text{O}_3\text{--CeO}_2$ showed no obvious variation compared to that in CeO_2 (Fig. S3a and b†). Additionally, the In 3d spectra of In_2O_3 showed two peaks at 451.7 (In $3d_{3/2}$) and 444.2 eV (In $3d_{5/2}$), while the binding energy of In 3d in $\text{In}_2\text{O}_3\text{--CeO}_x$ shifted positively about 1 eV compared to that of In_2O_3 (Fig. 2c). The results demonstrated the strong interaction between In_2O_3 and CeO_x , and electrons transferred from the crystalline In_2O_3 to amorphous CeO_x , which led to an increase in the proportion of Ce^{3+} in $\text{In}_2\text{O}_3\text{--CeO}_x$. Moreover, the linear sweep voltammetry (LSV) curves of In_2O_3 showed an obvious reduction peak at

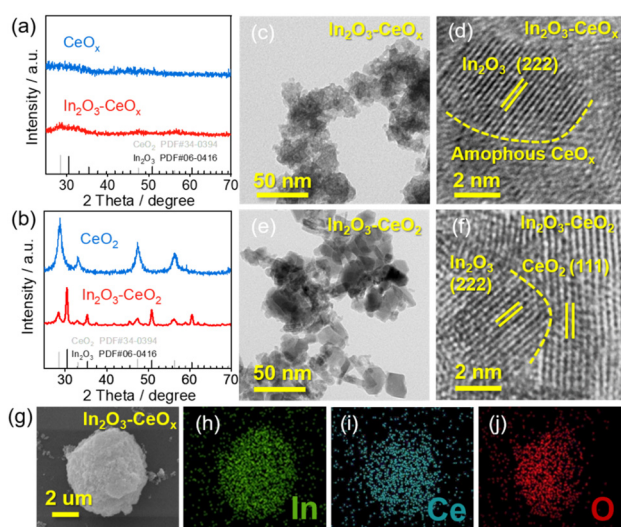


Fig. 1 (a) XRD patterns of CeO_x and $\text{In}_2\text{O}_3\text{--CeO}_x$, (b) XRD patterns of CeO_2 and $\text{In}_2\text{O}_3\text{--CeO}_2$, (c and d) HR-TEM image of $\text{In}_2\text{O}_3\text{--CeO}_x$ and (e and f) HR-TEM image of $\text{In}_2\text{O}_3\text{--CeO}_2$. (g–j) The corresponding EDX elemental mapping of $\text{In}_2\text{O}_3\text{--CeO}_x$.

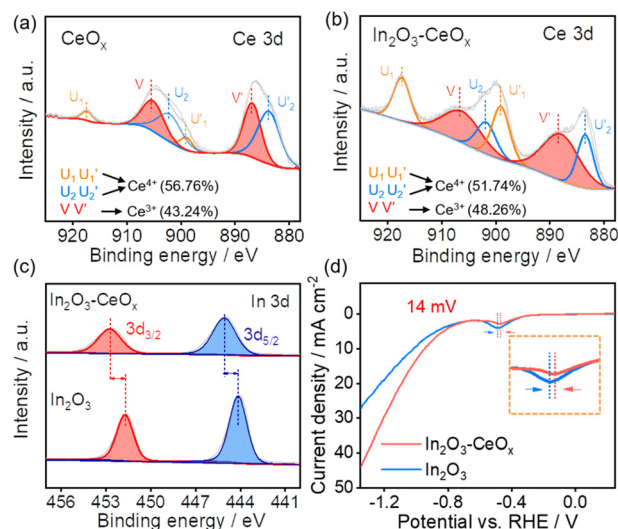


Fig. 2 Ce 3d XPS spectra of (a) CeO_x and (b) $\text{In}_2\text{O}_3\text{--CeO}_x$; (c) In 3d XPS spectra of $\text{In}_2\text{O}_3\text{--CeO}_x$ and In_2O_3 ; and (d) LSVs of In_2O_3 and $\text{In}_2\text{O}_3\text{--CeO}_x$ in CO_2 -saturated 0.5 M KHCO_3 at a scan rate of 50 mV s^{-1} .

−0.487 V (vs. RHE), corresponding to a typical $\text{In}^{3+}/\text{In}^0$ reduction peak (Fig. S4†).²⁷

It should be noted that the reduction peak potential of $\text{In}_2\text{O}_3\text{-CeO}_x$ positively shifted by 14 mV (appearing at −0.473 V) (Fig. 2d). The lower reduction potential of $\text{In}_2\text{O}_3\text{-CeO}_x$ meant an enhanced electrochemical redox activity.²⁸ In contrast, no obvious change in the reduction peak potential was detected for $\text{In}_2\text{O}_3\text{-CeO}_2$ compared to that of In_2O_3 (Fig. S3c†). This result was consistent with the XPS data, revealing that the crystalline–amorphous heterostructure of $\text{In}_2\text{O}_3\text{-CeO}_x$ led to stronger interactions between its individual components.

The electrocatalytic CO_2RR performances of In_2O_3 , $\text{In}_2\text{O}_3\text{-CeO}_x$, and $\text{In}_2\text{O}_3\text{-CeO}_2$ 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 (vs. RHE, all potentials used were vs. RHE unless otherwise stated). As depicted by the linear sweep voltammetry (LSV) curves of all catalysts (Fig. 3a and S5†), 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 $\text{In}_2\text{O}_3\text{-CeO}_x$ was larger than those of $\text{In}_2\text{O}_3\text{-CeO}_2$ and In_2O_3 in a CO_2 -saturated electrolyte, indicating that a crystalline–amorphous $\text{In}_2\text{O}_3\text{-CeO}_x$ 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 , $\text{In}_2\text{O}_3\text{-CeO}_2$ and $\text{In}_2\text{O}_3\text{-CeO}_x$ catalysts, CO and H_2 were detected as gas products, and formate was the

unique liquid product (Fig. S6†). The formate faradaic efficiency ($\text{FE}_{\text{formate}}$) of the three catalysts all exhibited a volcano-like pattern over the range of applied operating potentials, among which, the $\text{In}_2\text{O}_3\text{-CeO}_x$ electrode exhibited higher selectivity toward formate against H_2 and CO (Fig. 3b and c). More remarkably, the $\text{FE}_{\text{formate}}$ on the $\text{In}_2\text{O}_3\text{-CeO}_x$ electrode remained above 90% over a wide electrochemical window from −0.8 V to −1.2 V. The maximum $\text{FE}_{\text{formate}}$ reached 94.8% with a current density of 7 mA cm^{-2} at −0.9 V (Fig. 3c). By comparison, the maximum $\text{FE}_{\text{formate}}$ for $\text{In}_2\text{O}_3\text{-CeO}_2$ and In_2O_3 electrodes was only 74.2% and 73.6%, respectively, under −1.0 V (Fig. S7a and b†). The optimal electrolysis potential of $\text{In}_2\text{O}_3\text{-CeO}_x$ was more positive than that of In_2O_3 and $\text{In}_2\text{O}_3\text{-CeO}_2$, which suggested that lower electrical energy was required to cross the energy barrier and realize the CO_2RR by the $\text{In}_2\text{O}_3\text{-CeO}_x$ catalyst. Notably, H_2 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 $\text{In}_2\text{O}_3\text{-CeO}_x$ was tested by continuous electrolysis at −0.9 V. As shown in Fig. 3d, no evident decay of current density and $\text{FE}_{\text{formate}}$ was observed after 20 h-electrolysis, demonstrating the good stability of the prepared $\text{In}_2\text{O}_3\text{-CeO}_x$ electrode. Moreover, the LSV curves before and after long-term test showed no obvious difference (Fig. S8†), which further manifested the good stability of $\text{In}_2\text{O}_3\text{-CeO}_x$. After the test, the element mapping of $\text{In}_2\text{O}_3\text{-CeO}_x$ showed that In, Ce, and O were uniformly distributed (Fig. S9†). In addition, the HRTEM image of $\text{In}_2\text{O}_3\text{-CeO}_x$ after electrolysis still showed the amorphous morphology of CeO_x and the (222) plane of In_2O_3 (Fig. S9a and b†), indicating that the crystalline–amorphous heterostructure of $\text{In}_2\text{O}_3\text{-CeO}_x$ can be retained during the electrolytic process.

To gain a deeper understanding of the kinetics of CO_2 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). $\text{In}_2\text{O}_3\text{-CeO}_x$ presented a smaller calculated Tafel slope (176 mV dec^{-1}) compared to $\text{In}_2\text{O}_3\text{-CeO}_2$ (186 mV dec^{-1}) and pure In_2O_3 (375 mV dec^{-1}). The smallest Tafel slope of $\text{In}_2\text{O}_3\text{-CeO}_x$ suggested the largest increment in the CO_2 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, $\text{In}_2\text{O}_3\text{-CeO}_x$ showed smaller charge transfer resistance (R_{ct}) compared to $\text{In}_2\text{O}_3\text{-CeO}_2$ and In_2O_3 . The results suggested that the crystalline–amorphous heterostructure rendered faster charge transfer than the bare In_2O_3 and crystalline–crystalline heterostructure, and the interaction of electrochemically active In_2O_3 with the amorphous CeO_x 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).^{2,29,30} The ECSA of $\text{In}_2\text{O}_3\text{-CeO}_x$ (13.75 cm^2) was higher than those of $\text{In}_2\text{O}_3\text{-CeO}_2$ (11.50 cm^2) and In_2O_3 (9.50 cm^2), which can promote the electrocatalytic performance. In addition, the

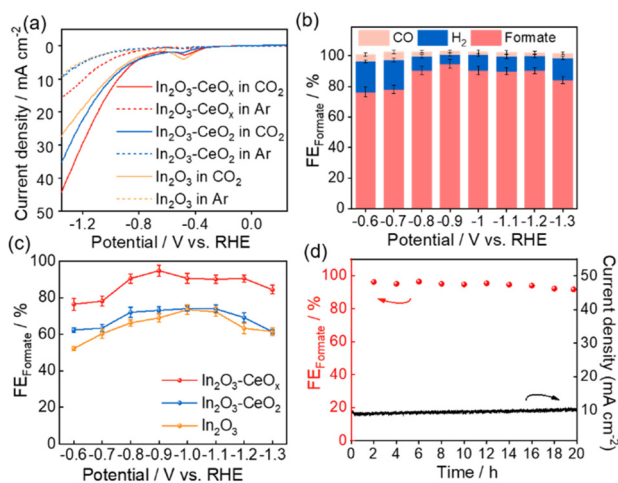


Fig. 3 CO_2 electroreduction in a 0.5 M KHCO_3 electrolyte. (a) LSV curves of $\text{In}_2\text{O}_3\text{-CeO}_x$, $\text{In}_2\text{O}_3\text{-CeO}_2$ and In_2O_3 electrodes in a CO_2 -saturated electrolyte. (b) The $\text{FE}_{\text{formate}}$, FE_{CO} and FE_{H_2} of $\text{In}_2\text{O}_3\text{-CeO}_x$ at different applied potentials, respectively. (c) $\text{FE}_{\text{formate}}$ of $\text{In}_2\text{O}_3\text{-CeO}_x$, $\text{In}_2\text{O}_3\text{-CeO}_2$ and In_2O_3 at different applied potentials, respectively. (d) Long-term stability of the CO_2 electroreduction for $\text{In}_2\text{O}_3\text{-CeO}_x$ at −0.9 V (vs. RHE).

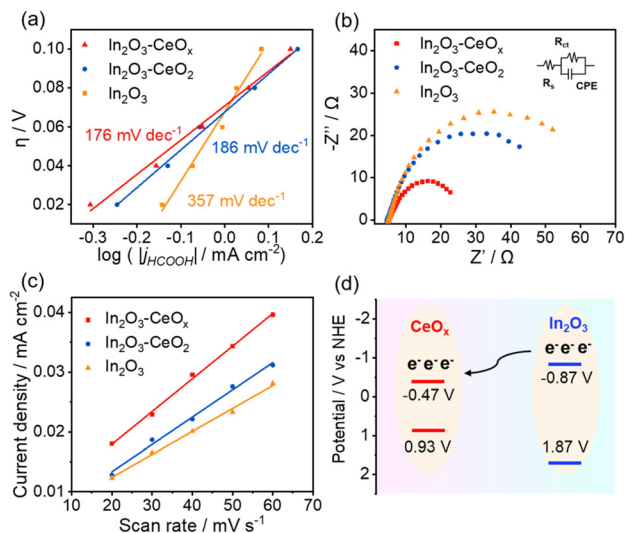


Fig. 4 Advantages of $\text{In}_2\text{O}_3\text{-CeO}_x$ for CO_2 reduction. (a) Tafel plots, (b) Nyquist plots (inset: equivalent circuit), (c) linear fitting of double-layer capacitive currents versus scan rates to estimate the ECSA of $\text{In}_2\text{O}_3\text{-CeO}_x$, $\text{In}_2\text{O}_3\text{-CeO}_2$ and In_2O_3 , and (d) schematic illustration of the charge transfer in $\text{In}_2\text{O}_3\text{-CeO}_x$.

partial current density of formate was normalized by the ECSA (Fig. S11†).² Similar to the geometric current density, the normalized current density of $\text{In}_2\text{O}_3\text{-CeO}_x$ was the highest among the three samples. The rough surface of the CeO_x substrate promoted the adsorption and dispersion of In_2O_3 , thereby increasing the active surface area. Furthermore, to verify the phenomenon of electron transfer between In_2O_3 and CeO_x in $\text{In}_2\text{O}_3\text{-CeO}_x$, we performed Mott-Schottky and valence band XPS experiments (Fig. S12†). As shown in Fig. 4d, the flat band potentials of In_2O_3 and CeO_x 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_2O_3 to CeO_x . However, the flat band and valence band potentials of CeO_2 and In_2O_3 were not significantly different (Fig. S13†), and thus electron transfer hardly occurred between CeO_2 and In_2O_3 .

Density functional theory (DFT) calculations were carried out to shed light on the origin of the enhanced activity of $\text{In}_2\text{O}_3\text{-CeO}_x$ for the CO_2RR (Fig. S14–S16†). The charge density difference and charge displacement curves of $\text{In}_2\text{O}_3\text{-CeO}_x$ and $\text{In}_2\text{O}_3\text{-CeO}_2$ 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 $\text{In}_2\text{O}_3\text{-CeO}_x$ heterostructure displayed a significant charge rearrangement around the crystalline–amorphous heterostructure interface, and electron transfer took place from In_2O_3 to CeO_x , 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 $\text{In}_2\text{O}_3\text{-CeO}_x$ is lower than that on $\text{In}_2\text{O}_3\text{-CeO}_2$ and In_2O_3 for the CO_2 -to-formate

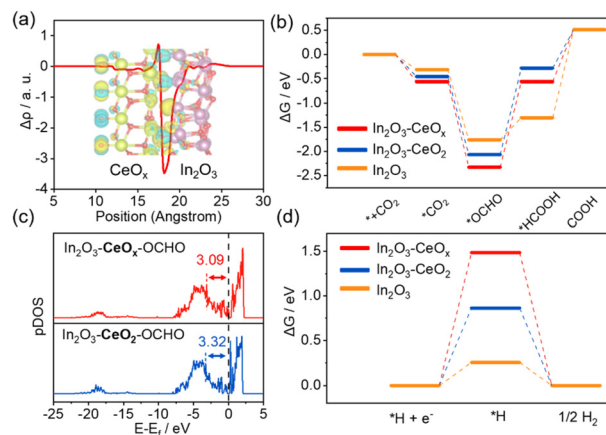


Fig. 5 DFT calculations. (a) Charge density difference and charge displacement curves of $\text{In}_2\text{O}_3\text{-CeO}_x$; purple, yellow, and red spheres represent In, Ce, and O atoms, respectively. (b) Gibbs free-energy diagrams of CO_2 -to-formate. (c) In-5p p-DOS of $\text{In}_2\text{O}_3\text{-CeO}_x$ and $\text{In}_2\text{O}_3\text{-CeO}_2$ after adsorbing $*\text{OCHO}$. (d) Gibbs free-energy diagrams of the HER.

process (Fig. 5b), suggesting that $\text{In}_2\text{O}_3\text{-CeO}_x$ was thermodynamically more favourable for CO_2 -to-formate conversion. The adsorption energies of the $*\text{OCHO}$ intermediates on $\text{In}_2\text{O}_3\text{-CeO}_x$ and $\text{In}_2\text{O}_3\text{-CeO}_2$ were further explained by the projected density of states (p-DOS). As shown in Fig. 5c, the centre of the p-band for $\text{In}_2\text{O}_3\text{-CeO}_x\text{-*OCHO}$ was closer to the Fermi level compared with that of $\text{In}_2\text{O}_3\text{-CeO}_2\text{-*OCHO}$, which verified that the antibonding state filling of the In-5p orbital of $\text{In}_2\text{O}_3\text{-CeO}_x$ is lower than that of $\text{In}_2\text{O}_3\text{-CeO}_2$, thereby enhancing the adsorption strength of $*\text{OCHO}$.¹⁴ In addition, the Gibbs free energy for the dominant competitive HER was also explored (Fig. 5d). The Gibbs free energy for generating $*\text{H}$ over $\text{In}_2\text{O}_3\text{-CeO}_x$ was much larger than that for $\text{In}_2\text{O}_3\text{-CeO}_2$ and In_2O_3 , indicating that the HER was more difficult to occur on $\text{In}_2\text{O}_3\text{-CeO}_x$. Therefore, the crystalline–amorphous $\text{In}_2\text{O}_3\text{-CeO}_x$ heterostructure accelerated the electron transfer, enhanced the adsorption to $*\text{OCHO}$, lowered the energy barrier for the process from OCHO^* to $*\text{HCOOH}$, and finally promoted the formation of the formate product. Furthermore, the $\text{In}_2\text{O}_3\text{-CeO}_x$ catalyst significantly suppressed the HER competition reaction compared with In_2O_3 and $\text{In}_2\text{O}_3\text{-CeO}_2$.

Conclusion

In conclusion, we described a facile strategy to fabricate the crystalline–amorphous $\text{In}_2\text{O}_3\text{-CeO}_x$ heterostructure and studied its performance for the CO_2RR . The experimental results showed that $\text{In}_2\text{O}_3\text{-CeO}_x$ achieved better catalytic performance than the crystalline–crystalline $\text{In}_2\text{O}_3\text{-CeO}_2$ heterostructure and In_2O_3 alone. The maximum FE of 94.8% was achieved on the $\text{In}_2\text{O}_3\text{-CeO}_x$ 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_2O_3 to amorphous CeO_x on the $\text{In}_2\text{O}_3\text{-}$

CeO_x heterostructure compared to the crystalline-crystalline In₂O₃-CeO₂ heterostructure, which decreased the interfacial charge transfer resistance. The In₂O₃-CeO_x 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 CO₂RR to formate. We believe that the work may provide an effective strategy for catalysing CO₂ conversion.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (22007004, 22178019, 21625101 and 21521005), the National Key Research and Development Program of China (2017YFB0307303) and the Fundamental Research Funds for the Central Universities (buctrc202010, XK1802-6, XK1803-05, XK1902 and 12060093063).

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