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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 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 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.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 $\rm CO_2$ 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 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.

Herein, crystalline-amorphous In₂O₃-CeO_x 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 In₂O₃-CeO_x, which was obviously more efficient than those of a pure In₂O₃ catalyst and a crystalline-crystalline In₂O₃-CeO₂ heterostructure. The improved performance of the In₂O₃-CeO_x catalyst was attributed to the electronic reconfiguration of indium by strengthened electron transfer between In2O3 and amorphous CeO_x, 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 CO₂RR to formate.

Results and discussion

The In₂O₃-CeO_r 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/H₂ flow for one hour to obtain the In₂O₃-CeO_x catalyst. The structures of the samples (e.g., In₂O₃-CeO_x, In₂O₃-CeO₂, the individual CeO_x, CeO₂ and In₂O₃) 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_r sample, which was caused by the small particle size and uniform dispersion of In₂O₃. In contrast, CeO₂ displayed the characteristic peaks of the crystal structure, which were consistent with those reported in the literature (Fig. 1b).²⁶ The

peaks of In₂O₃-CeO₂ matched well with the standard patterns of CeO₂ and In₂O₃, as shown in Fig. 1b. The high-resolution transmission electron microscopy (HR-TEM) images showed the crystalline-amorphous heterostructure interface of In₂O₃-CeO_x and crystalline-crystalline heterostructure interface of In₂O₃-CeO₂ (Fig. 1c-f). As shown in Fig. 1d, the lattice fringe of In₂O₃-CeO_x could be assigned to the (222) plane of In₂O₃ while the amorphous CeO_x 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 In₂O₃ 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 In₂O₃-CeO_x and In₂O₃-CeO₂ 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 Ce⁴⁺ and Ce³⁺ peaks (Fig. 2a), where Ce³⁺ 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_x (43.2%). In contrast, the proportion of Ce³⁺ in In₂O₃-CeO₂ showed no obvious variation compared to that in CeO₂ (Fig. S3a and b†). Additionally, the In 3d spectra of In₂O₃ 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 In_2O_3 -CeO_x shifted positively about 1 eV compared to that of In₂O₃ (Fig. 2c). The results demonstrated the strong interaction between In2O3 and CeO_x, and electrons transferred from the crystalline In₂O₃ 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

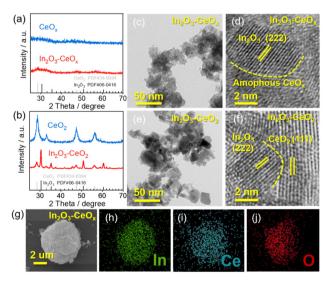


Fig. 1 (a) XRD patterns of CeO_x and $In_2O_3-CeO_{x_r}$ (b) XRD patterns of CeO_2 and $In_2O_3-CeO_2$, (c and d) HR-TEM image of $In_2O_3-CeO_x$ and (e and f) HR-TEM image of In₂O₃-CeO₂. (g-j) The corresponding EDX elemental mapping of In2O3CeOx.

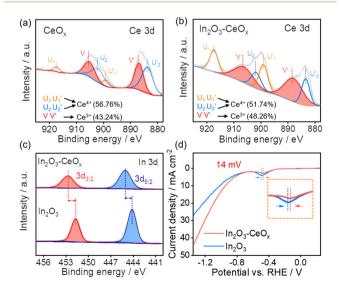


Fig. 2 Ce 3d XPS spectra of (a) CeO_x and (b) In₂O₃-CeO_x; (c) In 3d XPS spectra of ln_2O_3 -CeO_x and ln_2O_3 ; and (d) LSVs of ln_2O_3 and ln_2O_3 - CeO_x in CO_2 -saturated 0.5 M KHCO₃ at a scan rate of 50 mV s⁻¹.

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

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. ²⁸ 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 (νs . RHE, all potentials used were νs . 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 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

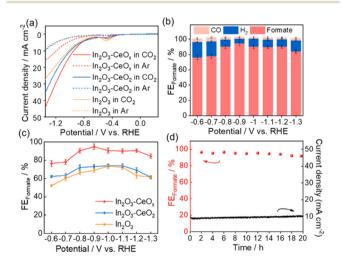


Fig. 3 CO $_2$ electroreduction in a 0.5 M KHCO $_3$ electrolyte. (a) LSV curves of $In_2O_3-CeO_x$, $In_2O_3-CeO_2$ and In_2O_3 electrodes in a CO $_2$ -saturated electrolyte. (b) The FE $_{formate}$, FE $_{CO}$ and FE $_{H_2}$ of $In_2O_3-CeO_x$ at different applied potentials, respectively. (c) FE $_{formate}$ 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_{formate}) 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_{formate} reached 94.8% with a current density of 7 mA cm $^{-2}$ at -0.9 V (Fig. 3c). By comparison, the maximum FE_{formate} for In₂O₃-CeO₂ and In₂O₃ electrodes was only 74.2% and 73.6%, respectively, under -1.0 V (Fig. S7a and b†). The optimal electrolysis potential of In₂O₃- 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_x catalyst. Notably, H₂ 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 In₂O₃–CeO_x was tested by continuous electrolysis at –0.9 V. As shown in Fig. 3d, no evident decay of current density and FE_{formate} was observed after 20 h-electrolysis, demonstrating the good stability of the prepared In₂O₃–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 In₂O₃–CeO_x. After the test, the element mapping of In₂O₃–CeO_x showed that In, Ce, and O were uniformly distributed (Fig. S9†). In addition, the HRTEM image of In₂O₃–CeO_x after electrolysis still showed the amorphous morphology of CeO_x and the (222) plane of In₂O₃ (Fig. S9a and b†), indicating that the crystalline–amorphous heterostructure of In₂O₃–CeO_x can be retained during the electrolytic process.

To gain a deeper understanding of the kinetics of CO₂ 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). In₂O₃-CeO_x 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⁻¹). The smallest Tafel slope of In_2O_3 -CeO_x suggested the largest increment in the CO₂ 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, In₂O₃-CeO_x showed smaller charge transfer resistance (R_{ct}) compared to In₂O₃-CeO₂ and In₂O₃. 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_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 In_2O_3 - CeO_x (13.75 cm⁻²) was higher than those of In₂O₃-CeO₂ (11.50 cm⁻²) and In₂O₃ (9.50 cm⁻²), which can promote the electrocatalytic performance. In addition, the

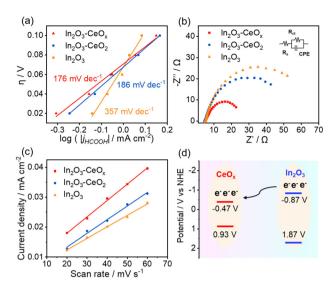


Fig. 4 Advantages of In₂O₃-CeO_x for CO₂ reduction. (a) Tafel plots, (b) Nyquist plots (inset: equivalent circuit), (c) linear fitting of double-layer capacitive currents versus scan rates to estimate the ECSA of In₂O₃-CeO_x, In₂O₃-CeO₂ and In₂O₃, and (d) schematic illustration of the charge transfer in In₂O₂-CeO₄

partial current density of formate was normalized by the ECSA (Fig. S11†).² Similar to the geometric current density, the normalized current density of In₂O₃-CeO_x was the highest among the three samples. The rough surface of the CeO_x substrate promoted the adsorption and dispersion of In₂O₃, thereby increasing the active surface area. Furthermore, to verify the phenomenon of electron transfer between In₂O₃ and CeO_x in In₂O₃-CeO_x, we performed Mott-Schottky and valence band XPS experiments (Fig. S12†). As shown in Fig. 4d, the flat band potentials of In₂O₃ 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 In₂O₃ to CeO_x. However, the flat band and valence band potentials of CeO₂ and In₂O₃ 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_x for the CO₂RR (Fig. S14-S16†). The charge density difference and charge displacement curves of In2O3-CeOx and In₂O₃-CeO₂ 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 In₂O₃-CeO_x heterostructure displayed a significant charge rearrangement around the crystalline-amorphous heterostructure interface, and electron transfer took place from In₂O₃ 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 In₂O₃-CeO_x is lower than that on In₂O₃-CeO₂ and In₂O₃ for the CO₂-to-formate

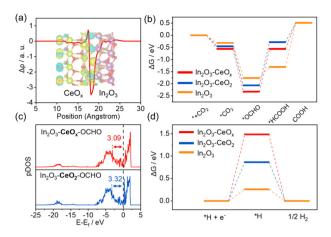


Fig. 5 DFT calculations. (a) Charge density difference and charge displacement curves of In₂O₃-CeO_x; purple, yellow, and red spheres represent In, Ce, and O atoms, respectively. (b) Gibbs free-energy diagrams of CO2-to-formate. (c) In-5p p-DOS of In2O3-CeOx and In2O3-CeO2 after adsorbing *OCHO. (d)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

process (Fig. 5b), suggesting that In₂O₃-CeO_x was thermodynamically more favourable for CO2-to-formate conversion. The adsorption energies of the *OCHO intermediates on In₂O₃-CeO_x and In₂O₃-CeO₂ were further explained by the projected density of states (p-DOS). As shown in Fig. 5c, the centre of the p-band for In₂O₃-CeO_x-*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 In₂O₃-CeO_x is lower than that of In₂O₃-CeO₂, 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 In₂O₃-CeO_r was much larger than that for In₂O₃-CeO₂ and In2O3, indicating that the HER was more difficult to occur on In₂O₃-CeO_x. Therefore, the crystalline-amorphous In₂O₃- 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 In₂O₃-CeO_x catalyst significantly suppressed the HER competition reaction compared with In₂O₃ and In₂O₃-CeO₂.

Conclusion

In conclusion, we described a facile strategy to fabricate the crystalline-amorphous In₂O₃-CeO_x heterostructure studied its performance for the CO2RR. The experimental results showed that In₂O₃-CeO_x achieved better catalytic performance than the crystalline-crystalline In₂O₃-CeO₂ heterostructure and In₂O₃ alone. The maximum FE of 94.8% was achieved on the In₂O₃-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 In₂O₃ to amorphous CeO_x on the In₂O₃-

 CeO_x heterostructure compared to the crystalline–crystalline In_2O_3 – CeO_2 heterostructure, which decreased the interfacial charge transfer resistance. The In_2O_3 – CeO_x heterostructure promoted the adsorption for *OCHO intermediates and thereby the energy barrier of *OCHO \rightarrow *HCOOH was reduced, which led to the high selectivity of the CO_2RR to formate. We believe that the work may provide an effective strategy for catalysing CO_2 conversion.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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