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Spatial regulation of Pt sites enables balanced hydrogen generation and electrochemical CO₂ reduction with the assistance of hydrogen spillover

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ABSTRACT

The electrocatalytic reduction of CO₂ to formate is emerging as a promising approach for industrial-scale CO₂ upgrading. In-based materials have been recognized as promising catalysts for this reaction because of their low toxicity and excellent selectivity; however, their low reactivity hinders their practical application. Beyond the conventional proton-coupled electron transfer (PCET) pathway, an alternative H⁺-mediated route has recently been proposed; however, its efficiency on In-based catalysts is hindered by sluggish H₂O dissociation and the competing hydrogen evolution reaction (HER). Herein, we demonstrate that the spatial modulation of Pt in In-based catalysts provides an effective strategy to precisely control H⁺ generation and utilization, thereby enhancing CO₂-to-formate efficiency. Although surface-deposited Pt substantially facilitates H₂O dissociation, excessive H⁺ accumulation leads to the undesired HER and lowers formate selectivity. By contrast, incorporated Pt strengthens CO₂ adsorption, enables balanced H⁺ generation, and reduces energy cost for H⁺ migration. As a result, Pt@In achieves a high formate Faradaic efficiency of 90% at −1.1 V, outperforming pure In (69%) and Pt/In (43%) under the same conditions. This work highlights the importance of spatially regulating hydrogen generation and transfer for designing highly selective CO₂ reduction electrocatalysts.

1. Introduction

As the greenhouse effect intensifies as a result of excessive CO₂ emissions, the research and development of CO₂ reclamation technologies are attracting global attention. [1–3] Among various strategies, the electrochemical CO₂ reduction reaction (CO₂RR) offers a promising approach to alleviate the energy crisis and reduce the CO₂ concentration in air. [4–10] Formate, one of the main products of the CO₂RR, is particularly attractive because of its feasible economic benefits and broad prospects in fuel cells and hydrogen storage. [11–13] As a result, great progress has been achieved in the CO₂RR to formate. Formate is produced via a two-electron reduction process. Metals such as Bi, [14–16] In, [17–19] and Sn, [20–22] which exhibit high overpotentials for the hydrogen evolution reaction (HER) and preferential binding to CO₂, have been demonstrated to achieve a high Faradaic efficiency (FE)

in the CO₂RR to formate. Among these reported catalysts, In-based catalysts have been widely investigated because of their low toxicity, superior ability to adsorb CO₂, and high selectivity toward formate. [23]

For the CO₂-to-formate reaction catalyzed by In-based catalysts, the first proton-coupled electron transfer (PCET) is known to be the rate-determining step (RDS) (CO₂ (ads) + H⁺ + e[−] → *OCHO). [24,25] Therefore, in recent years, substantial efforts, including morphology design, defect engineering, and ion doping, have been devoted to optimizing the electronic structure to favor CO₂ adsorption and to lower the energy barrier of this elementary step. However, most of the In-based catalysts still suffer from an unsatisfactory formate current density, highlighting the need for further development of advanced In-based catalysts.

In addition to the PCET process, another H⁺-mediated pathway has recently been reported to possibly be involved in the CO₂RR to formate.

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Specifically, reactive hydrogen species (H^*) are first generated via a Volmer step ($H_2O + M + e^- \rightarrow M - H^* + OH^-$) and subsequently migrate to CO_2 adsorption sites to form formate ($* + CO_2 + 2H^* \rightarrow * + HCOOH$). However, for Bi-, In-, and Sn-based catalysts, the Volmer step is sluggish because of its poor intrinsic H_2O dissociation ability, which requires large potentials to drive the reaction. [26] Several strategies have been proposed to enhance the H_2O activation ability of the catalysts to promote the CO_2 RR, including introducing sulfur species and depositing noble metals. Wang et al. demonstrated that sulfur-modified In could accelerate H_2O dissociation via the interaction between the chalcogenide and the hydrated cation, thereby facilitating H^* -mediated CO_2 RR to formate. [26] In addition, Lu et al. reported that Ru atom anchored on Bi facilitated H_2O activation and enabled efficient CO_2 hydrogenation at Ru–Bi bridge sites, resulting in enhanced formate production. [27] However, H_2 evolution remained inevitable and H_2 became the main product at high applied potentials as a result of H^* dimerizing or reacting with H_2O , limiting the real application of the catalyst. More importantly, although enhanced H^* generation has been demonstrated to promote the CO_2 RR to formate, the relationship between the extent of H^* supply and CO_2 RR selectivity remains unclear. It can be anticipated that excessive H^* generation will not lead to higher formate production because the surplus H^* tends to recombine into H_2 rather than migrating to CO_2 adsorption sites. Therefore, a key challenge is to precisely regulate the generation, transfer, and utilization of H^* so that hydrogen spillover can be selectively coupled with formate formation rather than HER. Achieving such a balance is crucial for maximizing formate selectivity and catalytic efficiency.

With this understanding, we modulated the spatial location of Pt in an In-based catalyst to precisely control H^* generation because Pt is known to exhibit excellent water dissociation capability. The CO_2 -to-formate conversion efficiency was evaluated as a function of the Pt location. We found that, compared with surface-deposited Pt, which led to excessive H^* generation and accelerated HER, the incorporated Pt facilitated moderate H^* generation accompanied by rapid hydrogen migration to CO_2 adsorption sites, thereby promoting CO_2 reduction to formate. As a result, Pt@In exhibited a high formate Faradaic efficiency of 90% at -1.1 V (all potentials are referenced to the reversible hydrogen electrode (RHE)) compared with pure In (69% at -1.1 V) and Pt/In (43% at -1.1 V). A combined approach of electrochemical techniques, kinetic isotope effect analysis, hydrogen trapping experiments, and theoretical calculations revealed that the superior performance originated from balanced H^* generation and efficient hydrogen spillover. This work provides a rational strategy for CO_2 electrocatalyst design through precise control of H^* generation and utilization.

2. Experimental

2.1. Materials and chemicals

All chemicals were used without further treatment: indium(III) chloride tetrahydrate ($InCl_3 \cdot 4H_2O$), chloroplatinic acid hexahydrate ($H_2[PtCl_6] \cdot 6H_2O$), sodium borohydride ($NaBH_4$), absolute ethanol (EtOH), potassium bicarbonate ($KHCO_3$), potassium hydroxide (KOH, $\geq 85.0\%$), and *t*-butyl alcohol ($(CH_3)_3COH$) were obtained from Nacalai Tesque. Urea ($(NH_2)_2CO$) and heavy water (D_2O) were purchased from Tokyo Chemical Industry. Deionized (DI) water was used for all of the solutions.

2.2. Synthesis of catalysts

(1) In and Pt@In. We first used a hydrothermal method to synthesize $In(OH)_3$ and $Pt@In(OH)_3$. [17] In a typical synthesis of $Pt@In(OH)_3$, 0.145 g of $InCl_3 \cdot 4H_2O$ and 2.18 mg of $H_2[PtCl_6] \cdot 6H_2O$ were dissolved in 30 mL of deionized water and 0.3 g of urea was subsequently added with magnetic stirring for 30 min. The solution was transferred to a Teflon-lined autoclave that was then sealed and heated in an oven at $140^\circ C$

for 12 h. After natural cooling to room temperature, the solid product was washed three times each with distilled water and EtOH and then dried under vacuum. The synthesis of $In(OH)_3$ followed the same procedure without the addition of $H_2[PtCl_6] \cdot 6H_2O$. The as-synthesized $In(OH)_3$ precursor was annealed at $500^\circ C$ for 2 h at a heating rate of $5^\circ C\ min^{-1}$ under an Ar gas flow. After annealing, the In_2O_3 sample (denoted as In) was obtained. $Pt@In_2O_3$ (denoted as Pt@In) was obtained by the same method under a mixed Ar/ H_2 gas flow. **(2) Pt/In.** Pt/In was synthesized via a chemical reduction method. Specifically, 30 mg of In was added into 20 mL of deionized water, followed by the addition of 0.8 mg of $H_2[PtCl_6] \cdot 6H_2O$ under magnetic stirring for 24 h. Subsequently, 1 mL of the freshly prepared $NaBH_4$ aqueous solution (containing 0.58 mg $NaBH_4$) was quickly added under vigorous stirring. After 1 h of reaction under stirring, the product was collected by centrifugation, washed with distilled water and EtOH, and finally dried under vacuum to obtain the Pt/In.

2.3. Characterization

We evaluated the structure of catalysts produced in this work by acquiring X-ray diffraction (XRD) data using a Rigaku Ultima IV X-ray diffractometer equipped with a Cu-K α radiation source. Transmission electron microscopy (TEM) and high-angle annular dark field scanning/transmission electron microscopy (HAADF-STEM) were performed to analyze the morphology and microstructure of the samples. These images were obtained using a H-800 Hitachi electron microscope and a JEOL ARM200F scanning transmission electron microscope, respectively. X-ray absorption fine structure (XAFS) measurements were performed at the BL01B1 beamline of the SPring-8 facility (JASRI, Harima, Japan), and the relevant data were analyzed using the ATHENA software. X-ray photoelectron spectroscopy (XPS) was performed using a Thermo Fisher Scientific Escalab 250Xi. All of the binding energies were referenced to the C 1 s peak of adventitious carbon (284.5 eV). Electron paramagnetic resonance (EPR) measurements were conducted on a JEOL RESONANCE JES-TE200 spectrometer. Inductively coupled plasma optical emission spectrometry (ICP-OES, Perkin-Elmer Optima 8300) was used to quantify the Pt content of the Pt@In and Pt/In catalysts. In situ ultraviolet–visible (UV–vis) absorption spectroscopic analyses were performed using a V-750 spectrophotometer (JASCO International). Prior to each measurement, the catalyst was mixed with WO_3 at a mass ratio of 1:24. During the analysis, changes in visible light absorption by the specimen were monitored while the material was heated from 25 to $400^\circ C$ under a H_2 atmosphere.

2.4. Electrochemical measurements

Electrochemical experiments were performed at room temperature using a conventional three-electrode configuration connected to an HZ-7000 electrochemical workstation (Hokuto Denko). Electrochemical CO_2 reduction was carried out in a two-compartment H-type cell in which the anodic and cathodic chambers were separated by a proton exchange membrane (Nafion 117, DuPont). Note that all subsequent electrochemical measurements were conducted in this reactor unless otherwise stated. A section of carbon paper coated with the catalyst specimen was used as the working electrode, and a Ag/AgCl (3.5 M KCl) electrode and Pt wire were used as the reference and counter electrodes, respectively. The working electrode was prepared by sonicating a mixture of 10 mg catalyst, 1 mL EtOH, and 0.05 mL Nafion (5 wt%) for 30 min to produce a homogeneous ink. A 0.1 mL portion of this ink was then applied to a $1 \times 1\ cm^2$ carbon paper substrate to give a mass loading of $1\ mg\ cm^{-2}$. 0.5 M $KHCO_3$ aqueous solution was used as the electrolyte for CO_2 electroreduction measurements. The potential conversion to RHE was performed using the equation without iR compensation: $E\ (vs.\ RHE) = E\ (vs.\ Ag/AgCl) + 0.208\ V + 0.059 \times pH$.

Prior to the electrochemical measurements, CO_2 was continuously bubbled through the electrolyte in each chamber at a flow rate of 20 mL

min^{-1} for no less than 30 min to eliminate dissolved air. After the chambers were saturated with CO_2 , the pH of the electrolyte was determined to be 7.3. The catalyst was pre-reduced at -1.5 V for 30 min. To evaluate the Faradaic efficiencies of the products, we quantified the gaseous products using a Shimadzu GC-8 A gas chromatograph and

analyzed the liquid products using a Shimadzu high-performance liquid chromatograph equipped with a Bio-Rad Aminex HPX-87H ion-exclusion column. In this work, CO and H_2 were the gaseous products, and formate was the main liquid product. The Faradaic efficiencies (FEs) of CO , H_2 , and formate production were calculated using the equation FE

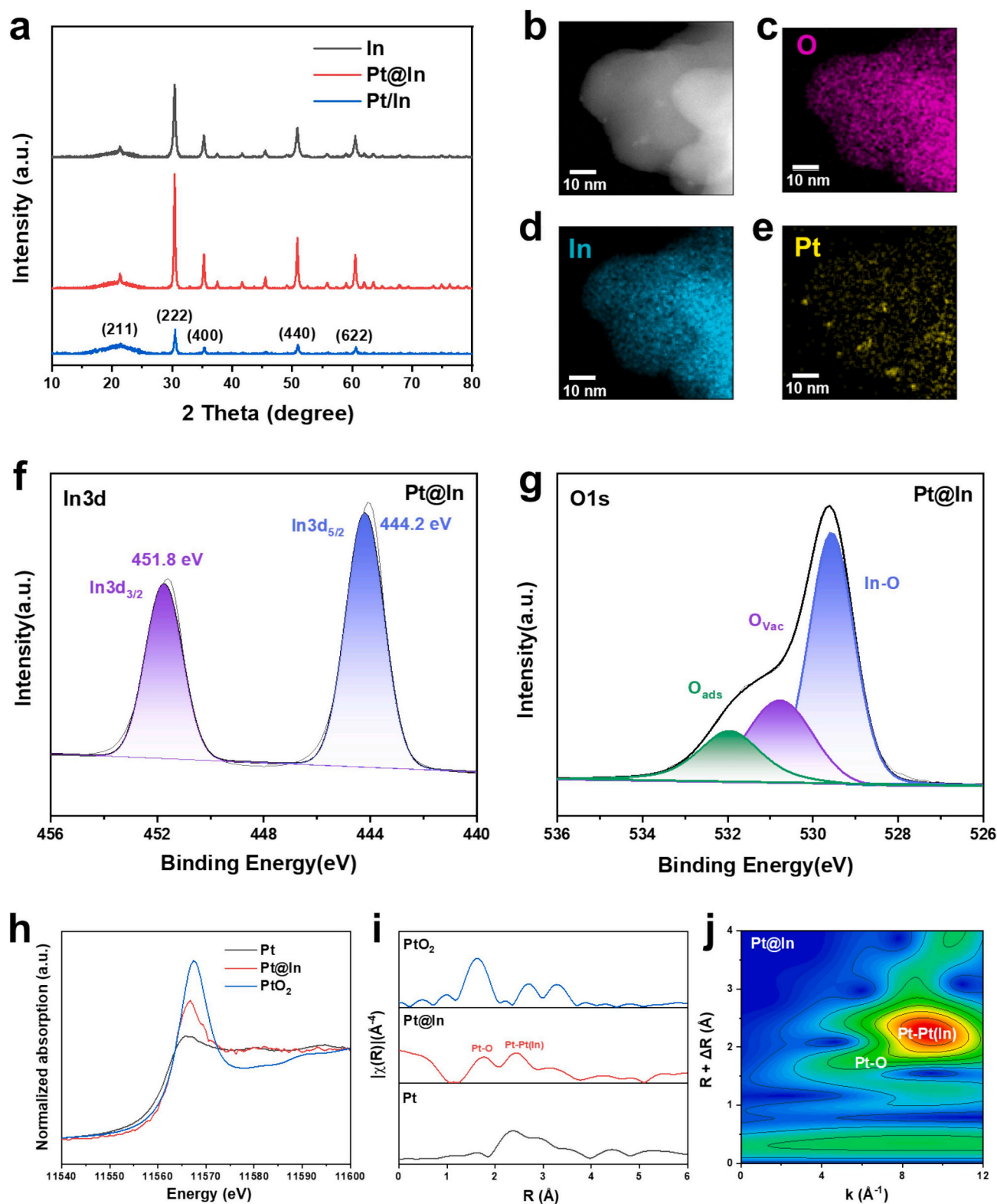


Fig. 1. (a) XRD patterns for In, Pt@In, and Pt/In. (b-e) STEM image and the corresponding elemental maps of Pt@In. (f) In 3d X-ray photoelectron spectroscopy (XPS) spectra of Pt@In. (g) O 1s XPS spectra of Pt@In. (h) Pt L₃-edge XANES spectra and (i) the k^3 -weighted Fourier transform EXAFS spectra of Pt@In and various reference materials. (j) Wavelet transform for the k^3 -weighted EXAFS spectra of Pt@In.

$= mF \times n/Q$, where m denotes the number of electrons required for the formation of the target product ($m = 2$ for CO, H₂, and formate), F represents the Faraday constant (96,485C mol⁻¹), n is the production amount (mol) for the final product, and Q is the total charge consumed during the electrochemical reaction.

Double-layer capacitance (C_{dl}) values were determined by recording cyclic voltammetry (CV) curves in the non-faradaic region at different scan rates. The C_{dl} values were then extracted by plotting $(j_a - j_c)/2$ as a function of the scan rate, where j_a and j_c are the positive and negative currents, respectively. Electrochemical impedance spectroscopy (EIS) measurements were performed over the frequency range from 0.1 Hz to 100 kHz using an AC perturbation of 10 mV. All experiments were carried out under ambient conditions.

2.5. DFT calculations

All DFT calculations were performed with the DMol³ program in the Materials Studio 17.2 software package. [28,29] The generalized gradient approximation (GGA) exchange-correlation functional proposed by Perdew, Burke, and Ernzerhof (PBE) was combined with the double numerical basis set plus polarization functions (DNP). A super-cell slab consisting of a 4 × 4 surface unit cell with three atomic (001) surface layers was adopted, with the bottom two layers fixed at the corresponding bulk positions and the top layers allowed to relax during geometry optimizations. The slab was separated by a vacuum space with a height of 30 Å. The Gibbs free-energy change (ΔG) was calculated at 298.15 K. The Gibbs free energy was given by $G = E + E_{ZPE} + \int C_p dT - TS$.

where E is the DFT-optimized total energy, E_{ZPE} is the zero-point energy, C_p is the heat capacity, $T = 298.15$ K is the temperature, and S is the entropy. Parameter E_{ad} was defined by the equation $E_{ad} = E_{ad-sorbate} + E_{slab} - E_{adsorbate/slab}$, where $E_{adsorbate}$ is the total energy of free adsorbate, E_{slab} is the total energy of the bare slab model, and $E_{adsorbate/slab}$ is the total energy of the adsorbate-slab system.

3. Results and discussion

3.1. Characteristics of catalysts

We analyzed the crystal structures of the as-prepared catalysts by acquiring their XRD patterns. The diffraction peaks at 21.3°, 30.4°, 35.3°, 50.9°, and 60.5° were observed in the patterns for all of the catalysts (Fig. 1(a)); these peaks could be ascribed to the (211), (222), (400), (440), and (622) crystal planes of cubic In₂O₃, respectively. [30] The XRD patterns for Pt@In and Pt/In were identical to that for In₂O₃, suggesting that the introduction of Pt did not change the phase structure. In addition, no distinctive peaks assigned to Pt or PtO₂ were observed in the XRD patterns of Pt@In and Pt/In, suggesting that no large crystalline Pt-containing phases were formed. We further examined the crystal structures after electrochemical activation to identify the actual structure during the CO₂RR (Fig. S1). In addition to the diffraction peaks originating from the carbon paper, three additional peaks at 32.9°, 39.2°, and 54.5° were observed in the patterns for all of the activated samples; these peaks could be assigned to the (101), (110), and (202) planes of metallic In, respectively. [31] These results demonstrated that In₂O₃ was completely reduced to metallic In after pretreatment. Notably, no diffraction peaks indexed to metallic Pt were detected for either Pt@In or Pt/In after activation, indicating the absence of significant Pt aggregation.

The microstructure of and elemental distribution within the catalysts were further investigated by STEM observations and energy-dispersive X-ray spectroscopy (EDX). HAADF-STEM images revealed that Pt@In exhibited an irregular nanoparticle morphology with an aggregated structure, very similar to the morphology of pristine In, indicating that the incorporation of Pt did not induce any noticeable change in the morphology of the catalyst. The corresponding elemental mapping results confirmed that In and O were homogeneously distributed

throughout the oxide framework (Fig. 1(b-e) and Fig. S2). Notably, no obvious agglomeration of the Pt was observed, implying that Pt was in a highly dispersed state. To further quantify the Pt dispersion, particle size statistical analysis was performed. The Pt species exhibited a narrow size distribution with an average diameter of 1.82 ± 0.04 nm, providing abundant evidence for the highly dispersed Pt species (Fig. S3). Collectively, the above results demonstrated that Pt-incorporated In₂O₃ was successfully prepared. By contrast, for Pt/In, some small Pt species were clearly observed on the particle surface, suggesting the successful deposition of Pt on In (Fig. S4).

To quantitatively determine the Pt content in the catalysts, ICP-OES measurements were performed (Table S1). The Pt contents in Pt@In and Pt/In were 0.5 and 0.6 wt%, respectively, indicating that the Pt amounts in Pt@In and Pt/In were comparable.

XPS was used to investigate the surface chemical states of the as-prepared samples. The In 3d spectrum (Fig. 1(f)) shows In 3d_{3/2} and In 3d_{5/2} peaks for In at binding energies of 451.7 and 444.1 eV, respectively, which were ascribed to In³⁺. [32] In comparison with the peak positions in the spectrum of pristine In (Fig. S5), those in the spectrum of In in Pt@In exhibited a slightly positive shift, suggesting an electronic interaction between Pt and In. The O 1s XPS spectra of the two samples were deconvoluted into three peaks (Fig. 1(g)), corresponding to lattice oxygen (In—O, ~529.6 eV), oxygen vacancies (~531.1 eV), and chemisorbed oxygen (~532.4 eV). [33] Notably, the relative ratio of oxygen vacancies to lattice oxygen increased from 0.42 for bare In to 0.45 for Pt@In, indicating that the incorporation of Pt led to a higher concentration of oxygen vacancies (Table S3). EPR measurements further confirmed the presence of oxygen vacancies, with Pt@In exhibiting a slightly stronger signal at $g \approx 2.00$ than pristine In, consistent with the XPS results (Fig. S6).

X-ray absorption spectroscopy was used to investigate the electronic and coordinative structure of Pt@In. Fig. 1h showed the Pt L₃-edge X-ray near-edge structure (XANES) spectra of Pt@In, together with those of Pt foil and PtO₂ as reference samples. The intensity of the white line in these spectra was associated with electron transitions from the 2p_{3/2} orbital to an unoccupied 5d orbital and reflects the Pt oxidation state. The white line intensity in the spectrum of Pt@In was intermediate between those in the spectra of metallic Pt and PtO₂, indicating that the average oxidation state of Pt in Pt@In was $+\delta$ ($0 < +\delta < 4$). The coordination environment of Pt in the In₂O₃ was further assessed by acquiring Pt L₃-edge Fourier-transformed k^3 -weighted extended X-ray absorption fine structure (EXAFS) spectra for this material as well as those for Pt foil and PtO₂ as references. The spectrum of Pt@In showed a first-shell feature centered at 1.7 Å, which was assigned to Pt—O bonding, [34] and a second-shell Pt—Pt(In) coordination feature at 2.4 Å (Fig. 1(i)). [35] To further explore the coordination environment of Pt, we conducted wavelet transform (WT) analysis to directly reveal the structure information in the resolution of R space and k space (Fig. 1(j)). The Pt@In exhibited a main WT intensity feature corresponding to Pt—Pt bonds, located at an R value of approximately 2.3 Å and a k value of ~ 9.3 Å⁻¹. This feature differed from the Pt—Pt metallic signal observed in the spectrum of Pt foil ($R \approx 2.7$ Å, $k \approx 9.7$ Å⁻¹, Fig. S7(b)), indicating that the Pt—Pt coordination environment in Pt@In was substantially modified by neighboring atoms, consistent with the XPS analysis results. In addition, a weaker WT signal corresponding to Pt—O bonds, located at an R value of approximately 1.6 Å and a k value of ~ 6.8 Å⁻¹, was observed. Collectively, these results confirmed that Pt species were incorporated into the In matrix rather than forming metallic Pt clusters.

3.2. Evaluation of electrochemical CO₂RR activity

To investigate the CO₂RR performance of the catalysts, we first conducted linear sweep voltammetry (LSV) experiments in a H-type three-electrode cell filled with 0.5 M KHCO₃ electrolyte. According to the XRD results, prior to the CO₂RR tests, all of the In₂O₃ catalysts were

reduced to metallic In after the pretreatment at -1.5 V (all potentials were referenced to the reversible hydrogen electrode (RHE)) for 30 min. As shown in Fig. 2(a), in Ar-saturated electrolyte, the current densities for Pt@In and Pt/In were higher than that for pure In, indicating that Pt played an important role in accelerating H_2O dissociation. Notably, Pt@In showed a much lower enhancement compared with Pt/In. By comparison, in CO_2 -saturated electrolyte, the onset potentials for In and Pt@In shifted to more positive values and the current densities increased dramatically, indicating that the catalysts strongly favored the CO_2RR over the HER. However, the current density for the Pt/In catalyst in the CO_2 -saturated electrolyte was markedly lower than that in the Ar-saturated electrolyte, suggesting that the spatial location of Pt would strongly influence the CO_2RR behavior.

To identify and quantify the CO_2RR products, we investigated the catalytic performance at different cathodic potentials between -0.9 and -1.2 V. Gaseous and liquid products were analyzed by gas chromatography (GC) and liquid chromatography (LC), respectively. Formate and H_2 were detected as the main products over all of the catalysts. As shown in Fig. 2(b), In exhibited moderate formate selectivity, with a maximal $\text{FE}_{\text{Formate}}$ of 69% at -1.1 V. By comparison, Pt@In displayed remarkably enhanced selectivity toward formate production, achieving 90% at -1.1 V. However, the $\text{FE}_{\text{Formate}}$ for Pt/In was much lower than those for In and Pt@In, and H_2 was the dominant product at -1.1 and -1.2 V.

The partial current density for formate allowed us to accurately compare the CO_2 -to-formate activity of the catalysts (Fig. 2(c)). The FEs of CO and H_2 were also evaluated (Fig. S10). Pt@In showed the highest performance (22 mA at -1.2 V) among the three catalysts between -0.9 and -1.2 V; this formate current density was more than twofold higher than those of pristine In (10.3 mA) and Pt/In (7.8 mA) at -1.2 V. These results provide solid evidence that the synergistic interaction between Pt and In effectively suppressed the undesired HER and promoted the conversion of CO_2 to formate when Pt species were properly incorporated within In clusters (Fig. 2(c)). By contrast, when Pt species were deposited onto the In surface, the HER was dominant. This comparison clearly demonstrated that the spatial location of Pt governed the CO_2RR performance. The above results suggested that Pt@In exhibited competitive formate selectivity and activity compared with representative In-based CO_2RR -to-formate catalysts reported in previous studies (Table S4). [24,36–41]

In addition to demonstrating its excellent activity, we examined the durability of Pt@In via long-term electrolysis performed at -1.1 V. Pt@In maintained a steady current and $\sim 85\%$ $\text{FE}_{\text{Formate}}$ after 22 h (Fig. 2(d)). However, a gradual decline in both current density and formate selectivity was observed during extended operation, and the $\text{FE}_{\text{Formate}}$ decreased to approximately 80% and 60% after 43 h and 50 h, respectively (Fig. S11).

To investigate the origin of this deactivation, XRD patterns were

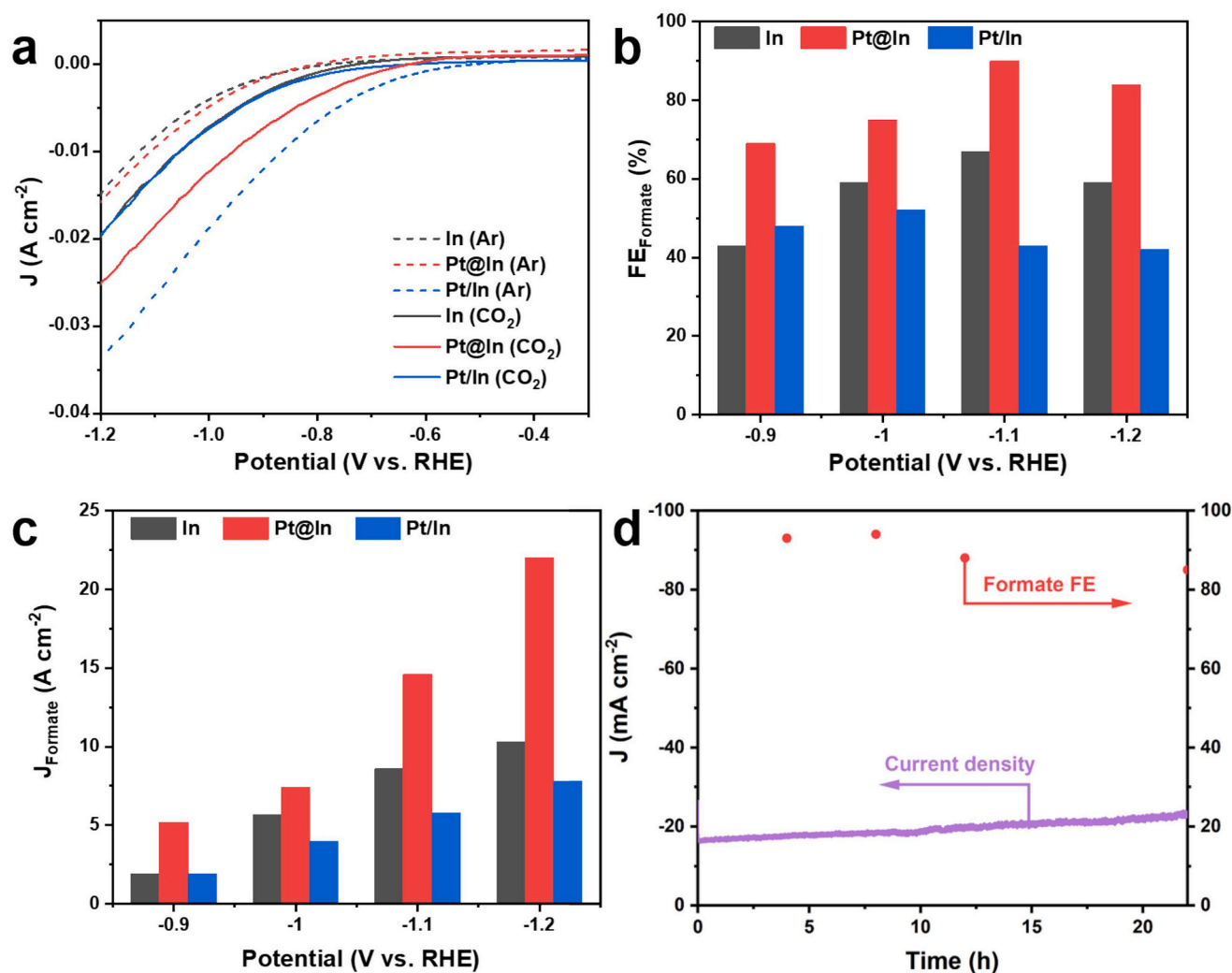


Fig. 2. (a) LSV polarization curves in Ar and CO_2 -saturated 0.5 m KHCO_3 , (b) Comparison of formate FE at various applied potentials. The FEs of the products were taken after 30 min electrolysis, (c) Partial current densities for formate of prepared catalysts, (d) Durability via i-t-test of Pt@In in the H-cell configuration for 22 h at -1.1 V.

collected after different electrolysis durations (Fig. S12). Even after 50 h of operation, the catalyst retained the metallic In phase, and no detectable diffraction peaks corresponding to metallic Pt were observed, indicating the absence of significant Pt aggregation during electrolysis. However, a gradual decrease in diffraction intensity was observed with increasing electrolysis time. The gradual loss of crystallinity might originate from partial dissolution and reconstruction of surface In species. In addition, the accumulation of adsorbed intermediates could obstruct active sites and inhibit hydrogen transfer and CO₂ activation, resulting in reduced activity and FE_{Formate} during long time operation.

3.3. Mechanism

Pt@In displayed a remarkable enhancement in CO₂RR performance compared with bare In and Pt/In. To elucidate the origin of this improvement and exclude the contributions from conductivity differences and variations in the number of active sites, we conducted the following experiments. Nyquist plots of the EIS data revealed that the charge-transfer resistance of the catalyst decreased substantially after Pt was introduced (Fig. S13). Although Pt/In exhibited the lowest resistance (5.5 Ω), its total current in the LSV conducted in CO₂-saturated electrolyte was comparable to that of In, indicating that although Pt

incorporation improved the interfacial charge-transfer kinetics, the superior performance of Pt@In cannot be solely attributed to reduced charge-transfer resistance. In addition, the double-layer capacitance (C_{dl}) values were linearly correlated with the electrochemical surface area (ECSA), and C_{dl} values could be obtained from cyclic voltammograms acquired at different scanning rates in the non-Faradaic region (Fig. S14). The measured C_{dl} values were 0.236, 0.237, and 0.328 mF cm⁻² for In, Pt@In, and Pt/In, respectively. The negligible difference in C_{dl} was attributable to the low incorporation or loading amount of Pt, which did not substantially alter the concentration of active sites. Accordingly, the calculated ECSA values for In, Pt@In, and Pt/In were 4.72, 4.74, and 6.56 cm², respectively (assuming the specific capacitance was 50 mF cm⁻²). After normalization relative to the ECSA values, Pt@In still exhibited the highest formate partial current densities, indicating that its superior CO₂RR performance cannot be solely attributed to an increase in its ECSA (Fig. S15).

In previous studies, for CO₂-to-formate catalyzed by In-based catalysts, in addition to the PCET pathway, an alternative H⁺-mediated pathway had also been proposed, in which H₂O dissociation was considered to be a kinetically slow step. Therefore, we speculated that the promoted CO₂RR performance of Pt@In might originate from accelerated H₂O dissociation induced by Pt. We tested this hypothesis by

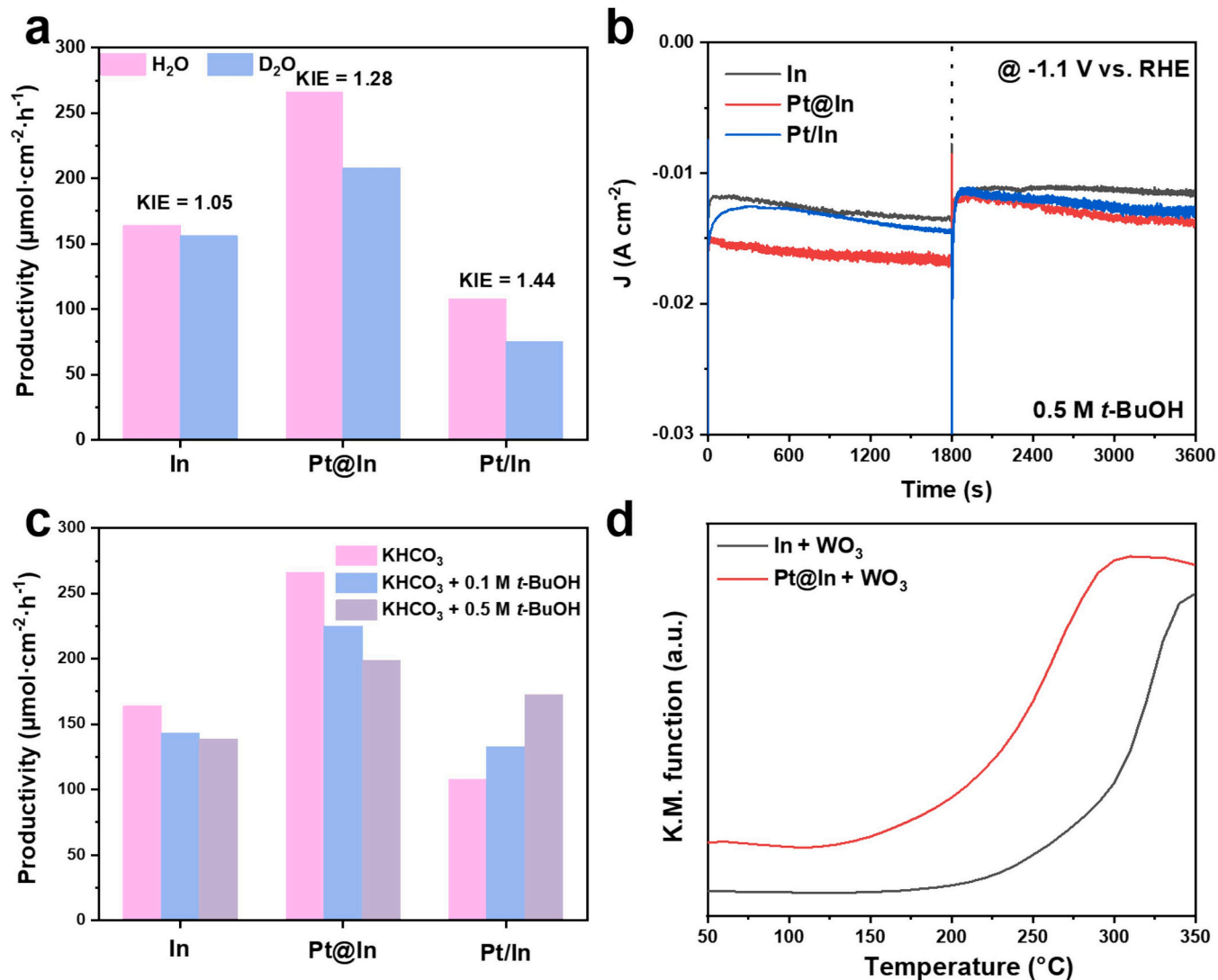


Fig. 3. (a) Comparison of the formate productivity over In, Pt@In and Pt/In in CO₂-saturated KHCO₃ – H₂O solution and a CO₂-saturated KHCO₃ – D₂O solution, (b) LSV curves and (c) the corresponding formate productivities of different catalysts at -1.1 V in a CO₂-saturated 0.5 M KHCO₃ solution with 0.5 M t-BuOH, (d) Changes in the visible light absorption properties of In and Pt@In with temperature.

conducting kinetic isotope effect (KIE) experiments for H/D using H₂O and D₂O as the proton sources over In, Pt@In and Pt/In catalysts. [26,27] When D₂O was substituted for H₂O in 0.5 M KHCO₃ electrolyte, formate in the form of DCOOH was produced. The KIE values of In, Pt@In, and Pt/In were determined to be 1.05, 1.28, and 1.44, respectively (Fig. 3(a)). The KIE value for pristine In was close to 1, suggesting that the H₂O dissociation step played a minor role in the reaction kinetics and that In might mainly follow the PCET pathway because of the poor H₂O activation ability. In contrast, the larger KIE values observed for Pt@In and Pt/In indicated that hydrogen-related processes (including H₂O activation and subsequent H⁺ migration) played an important role after Pt introduction. Notably, Pt/In exhibited the largest KIE value, implying a stronger involvement of hydrogen-related steps in the reaction kinetics. These results further supported the involvement of H⁺-mediated mechanism in Pt-containing catalysts.

We also investigated the effect of the electrolyte pH on the CO₂RR over In and Pt@In catalysts because H₂O activation would become more difficult at higher pH (Fig. S16). Two electrolytes were used to regulate the local pH: pH of KHCO₃ + H₂SO₄ (6.5) < pH of KHCO₃ (7.3). The formate formation rate for the two catalysts in KHCO₃ was much higher than that in KHCO₃ + H₂SO₄, indicating that a higher local pH favored formate formation. In addition, the ratio of the formate formation rate over Pt@In to that over In decreased in the order of Rate(Pt@In)/Rate(In) in KHCO₃ (1.62) > Rate(Pt@In)/Rate(In) in KHCO₃ + H₂SO₄ (1.42), suggesting that promoting H₂O dissociation could indeed accelerate the electrochemical CO₂RR to produce formate. [31,42]

In addition, we investigated the enhanced generation of H⁺ by adding *t*-butanol (*t*-BuOH), which was reported to trap H⁺ species, to the electrolyte. [27,43,44] After the addition of 0.1 M *t*-BuOH, only slight decreases in current density were observed for all three catalysts, and the magnitude of current decay was similar among In, Pt@In, and Pt/In (Fig. S17). This result suggested that the generated H⁺ was only partially trapped at low *t*-BuOH concentration. When higher concentrations of *t*-BuOH (0.5 M) were introduced, a substantially larger decay in current density was observed over Pt@In and Pt/In compared with that over pristine In (Fig. 3(b)). This pronounced current decay suggested that the introduction of Pt promoted a high concentration of H⁺, indicating a stronger involvement of H⁺-mediated processes on the Pt-containing catalysts. To gain deeper mechanistic insights into the role of H⁺ in formate formation and into the differences among the catalysts, we further analyzed the corresponding formate productivities before and after the addition of *t*-BuOH. For bare In, the formate formation rate only exhibited a slight decrease after the addition of *t*-BuOH, indicating limited participation of H⁺ in the reaction. For bare In, the formate formation rate only exhibited a slight decrease after the addition of either 0.1 M or 0.5 M *t*-BuOH, indicating the limited participation of H⁺ in the reaction. By contrast, for Pt@In, the *t*-BuOH addition led to a much larger decrease in formate productivity, suggesting that H⁺ species played a critical role in promoting formate formation over Pt@In. Interestingly, for Pt/In, the introduction of *t*-BuOH resulted in a substantial suppression of H₂ production, accompanied by an increase in formate formation. This behavior was attributable to the excessive surface H⁺ coverage on Pt/In before *t*-BuOH was added, which favored the HER. After H⁺ capture, the excessive H⁺ coverage was reduced, inhibiting the HER and allowing more CO₂ to participate in formate formation. These results further highlighted that the optimal CO₂RR performance did not rely on the maximum H⁺ generation capability but rather on a balanced H⁺ supply regulated by appropriate spatial location of Pt, which governed the H⁺ concentration and the reaction selectivity.

In addition to H⁺ generation, H⁺ spillover was also responsible for the CO₂ hydrogenation to form HCOO[−]—a key intermediate in formate production. WO₃ has often been used as an effective probe for the hydrogen spillover phenomenon to evaluate the electron diffusion behavior of catalysts. [45,46] The hydrogen atoms generated via H₂ adsorption on metal sites were known to eventually migrate onto the WO₃ surface, where they were dissociated into protons and electrons.

The transferred electrons subsequently reduced W⁶⁺ to W⁵⁺, accompanied by a visible color change of WO₃ from yellow to blue, whereas the protons interacted with surface anions. In the present work, we studied the extent of electron diffusion accompanying hydrogen spillover by acquiring in situ UV–vis spectra from a physical mixture of WO₃ and the catalysts under a H₂ atmosphere (Fig. 3(d)). Combinations of WO₃ and In exhibited visible-light absorption at ~200 °C. By comparison, WO₃ mixed with Pt@In showed visible-light absorption even at room temperature. This effect was attributable to the increased concentration of oxygen vacancies induced by the incorporation of Pt into the In₂O₃, which was verified by XPS measurements. These oxygen vacancies both enhanced electron diffusion and accelerated the hydrogen transfer kinetics. As a result, WO₃ mixed with Pt@In exhibited stronger light absorption beginning at ~130 °C, as evidenced by the sample changing from yellow to dark-blue, confirming that the WO₃ was reduced. [47]

To further investigate the hydrogen transfer behavior of the catalysts in their real working state, we further examined the electrochemically activated samples (Fig. S19). After the pretreatment, a pronounced enhancement in visible-light absorption was observed, further suggesting the successful reduction of In₂O₃ to metallic In. Notably, the pretreated Pt@In showed a much stronger optical absorption at ~300 °C. By comparison, the change in absorption of pristine In was relatively limited. These reducing experiments suggested that metallic In possessed a relatively weak H₂ activation and hydrogen transfer ability, whereas the incorporation of Pt substantially promoted H₂ dissociation and subsequent hydrogen spillover.

3.4. DFT calculations

To further understand the enhanced performance of the CO₂RR to formate over the Pt@In catalyst, we carried out DFT calculations. Notably, In₂O₃ would be reduced to metallic In during the CO₂RR pretreatment; therefore, In(001), Pt-incorporated In(001), and Pt deposited on In(001) were constructed as the catalyst models (Fig. 4(a–c)). Prior to determining the reaction Gibbs free energy, we first examined the electronic properties of the catalysts. The work function of Pt@In and Pt/In were calculated to be 3.68 and 3.86 eV (Fig. S20), which were much lower than that of pure In (4.10 eV). Notably, the lower work function of Pt@In compared with that of Pt/In indicated that incorporated Pt was more effective in promoting charge transfer than surface-deposited Pt, [48] which might partially account for the superior CO₂RR activity of Pt@In.

Given that CO₂ adsorption was a prerequisite for the CO₂RR, we first evaluated the adsorption energies for CO₂ on the three catalysts. The In and Pt/In exhibited relatively weak CO₂ adsorption (Fig. 4(d)). By contrast, incorporated Pt substantially promoted CO₂ adsorption, and the enhanced CO₂ adsorption on the Pt@In catalyst was further confirmed experimentally through OH[−] adsorption. The dissolved OH[−] ions in a 0.1 M KOH electrolyte was usually used as a surrogate to evaluate the adsorption strength of active *CO₂[−] intermediates (Fig. S21). [49] The more negative adsorption potential of Pt@In indicates an enhanced binding affinity with OH[−], thus implying an optimized stabilizing capacity with *CO₂[−] compared to that with other counterparts. In addition, because H₂O adsorption played an important role in subsequent activation and H⁺ formation, the adsorption energies of H₂O on the three catalysts were also investigated (Fig. 4(e)). The introduction of Pt enhanced H₂O adsorption, following the order Pt/In > Pt@In > In. A stronger interaction with H₂O was expected to facilitate H₂O dissociation and H⁺ generation.

On the basis of the adsorption characteristics of H₂O and CO₂, we further evaluated the Gibbs free energy landscapes for CO₂ reduction to formate over different catalysts to elucidate the role of incorporated Pt in promoting CO₂RR performance. In the first step, adsorbed H₂O was dissociated to H⁺ via a Volmer step. Pristine In exhibited an almost thermoneutral Gibbs free energy change ($\Delta G \approx -0.03$ eV) (Fig. 4(g)), indicating a limited thermodynamic driving force for H⁺ generation.

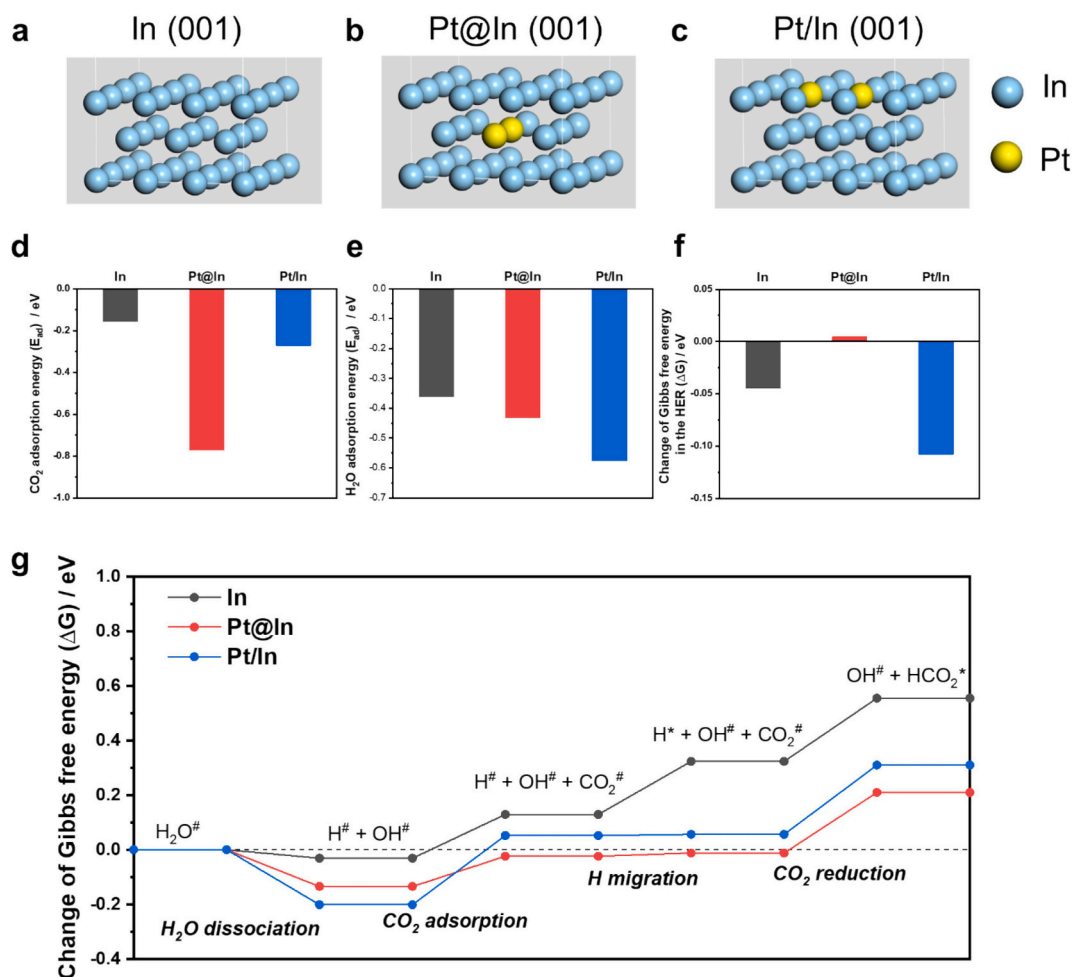


Fig. 4. Geometrical absorption models for (a) In, (b) Pt@In and (c) Pt/In, where the balls in blue and yellow represent Indium and Platinum, (d) CO₂ and (e) H₂O adsorption energy over different catalysts, (f) Changes of Gibbs free energy in the HER, (g) Change of Gibbs free energy for CO₂ reduction to formate.

This result was consistent with its poor H₂O activation ability and further suggested that H^{*} formation on In was not favored. Upon the introduction of Pt, the free energy change for H₂O dissociation was substantially reduced to -0.13 eV over Pt@In and further to -0.20 eV over Pt/In, demonstrating that the introduction of Pt markedly facilitated H₂O dissociation. In particular, for Pt/In, surface-deposited Pt shifted the H₂O dissociation site from In to Pt, resulting in excessive H^{*} generation and a high HER tendency. By contrast, incorporating Pt provided a more balanced H^{*} generation, which was beneficial for the CO₂RR to formate. The generated H^{*} then migrated to a CO₂ adsorption site for subsequent hydrogenation. The H^{*} migration on pristine In required a ΔG value of 0.19 eV, implying that H^{*} transfer was thermodynamically unfavorable. This high energy cost, together with its poor H₂O dissociation ability, explained why In mainly followed the PCET pathway rather than the H^{*}-mediated route. The ΔG for H^{*} migration decreased to 0.01 and 0.004 eV over Pt@In and Pt/In, respectively. Such low ΔG values indicate that H^{*} transfer becomes thermodynamically more favorable after Pt incorporation. Although explicit transition-state calculations were not performed in the present work, the reduced free-energy difference suggests an enhanced driving force for H^{*} relocation toward CO₂ adsorption sites. CO₂ reduction was the RDS for all of the catalysts. The ΔG for HCOO^{*} formation over Pt@In was 0.22 eV, which was lower than that over In (0.23 eV) and Pt/In (0.25 eV), further demonstrating that incorporated Pt favored the conversion to formate.

We also investigated the ΔG associated with the recombination of H^{*} to H₂. Pristine In exhibited a ΔG value of -0.04 eV (Fig. 4(f)), indicating that H₂ formation via H^{*} recombination was thermodynamically

feasible. After Pt was deposited onto In, the ΔG for hydrogen evolution sharply decreased to -0.11 eV, suggesting that H^{*} was prone to recombine to form H₂ rather than migrate to CO₂ adsorption sites, consistent with the experimental results. By contrast, the ΔG increased to 0.005 eV over Pt@In, demonstrating that the incorporation of Pt suppressed H₂ evolution effectively, accounting for the high FE_{Formate} over Pt@In.

A plausible mechanism based on the experimental results and DFT calculations was shown in Fig. 5. For pristine In, the limited thermodynamic driving force for H^{*} generation, together with high cost of H^{*} migration, made a H^{*}-mediated process unfavorable. Therefore, bare In tended to follow the PCET pathway to produce formate. For Pt/In, surface-deposited Pt substantially accelerated H₂O dissociation and H^{*} migration, leading to a markedly enhanced H^{*} supply. However, because of relatively weak CO₂ adsorption, excessive H^{*} generated on Pt could not entirely migrate to CO₂ adsorption sites and was prone to recombine into H₂, thereby promoting the undesired HER and lowering FE_{Formate}. By contrast, incorporated Pt significantly promoted CO₂ adsorption. Meanwhile, incorporating Pt provided a more balanced H^{*} generation and substantially reduced the energy cost for H^{*} migration. The higher local CO₂ coverage facilitated efficient trapping of migrated H^{*}, which efficiently inhibited H₂ evolution and led to enhanced formate production.

4. Conclusion

In summary, we demonstrated that the CO₂-to-formate performance

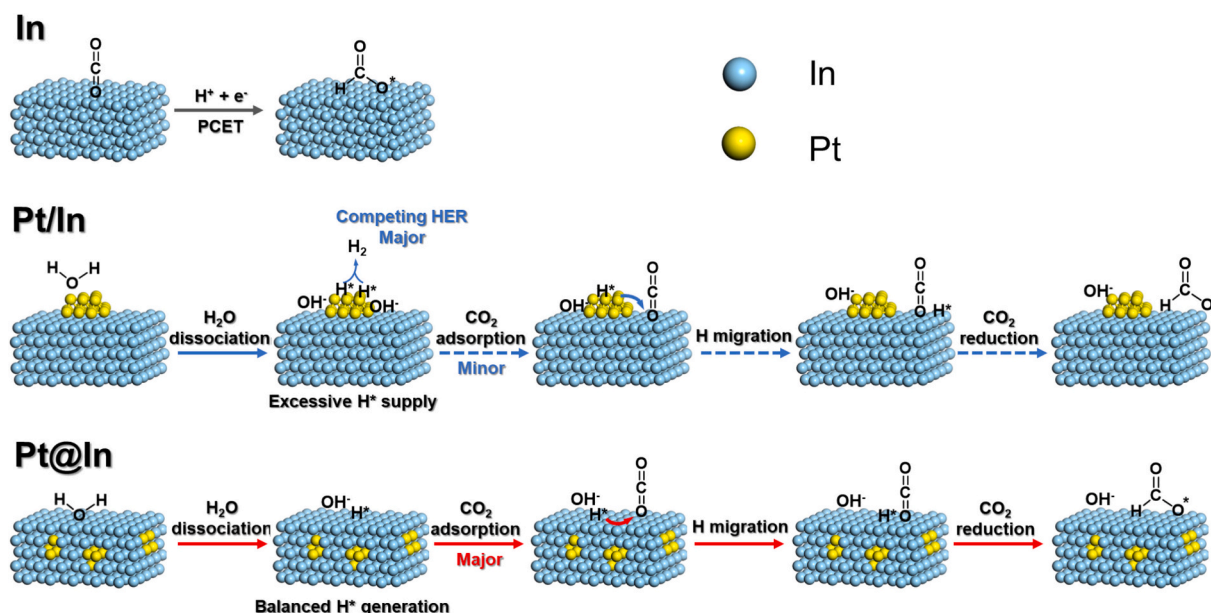


Fig. 5. Schematic illustration of the path of CO₂ reduction to formate on In, Pt/In and Pt@In, where the balls in blue and yellow represent Indium and Platinum.

of In-based catalysts could be improved with appropriate spatial modulation of Pt in the catalysts. Although surface-deposited Pt substantially promoted H₂O dissociation, excessive generation of H⁺ inevitably led to the competing HER. By contrast, incorporating Pt within the In matrix facilitated moderate H⁺ accumulation accompanied by rapid hydrogen migration to CO₂ adsorption sites, thereby promoting CO₂ reduction to formate. As a result, compared with pure In and Pt/In, Pt@In exhibited superior CO₂RR performance (FE_{Formate} of 90% at −1.1 V) and excellent long-term stability. Comprehensive electrochemical experiments and further DFT calculations revealed that the enhanced performance arose from balanced H⁺ generation and efficient hydrogen spillover. Our study provided a mechanistic insight that was important for the design of high-CO₂RR-performance electrocatalysts, especially those that follow a H⁺-mediated pathway.

CRedit authorship contribution statement

Tianhan Shen: Writing – original draft, Investigation, Formal analysis, Data curation, Conceptualization. **Kaining Li:** Methodology. **Kazuki Shun:** Validation. **Yoshifumi Kondo:** Investigation. **Yasutaka Kuwahara:** Validation. **Tohru Sekino:** Validation. **Yun Hu:** Funding acquisition. **Kohsuke Mori:** Writing – review & editing, Supervision, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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providing XAFS data were performed at the BL01B1 beamline within the SPring-8 facility with the approval of JASRI (proposal nos. 2025B1567 and 2025A1703).

Appendix A. Supplementary data

The following are the Supplementary data to this article: **Fig. S1.** XRD pattern of In, Pt@In and Pt/In after activation. **Fig. S2.** STEM image and the corresponding elemental maps of Pt@In sample. **Fig. S3.** STEM images and the corresponding statistical analysis of the Pt particle size. **Fig. S4.** TEM images of In, Pt@In and Pt/In. **Fig. S5.** In 3d X-ray and O 1 s photoelectron spectroscopy (XPS) spectra of In. **Fig. S6.** Electron paramagnetic resonance (EPR) spectra of In and Pt@In. **Fig. S7.** (a) Pt L₃-edge EXAFS fitting curves, (b) Pt L₃-edge FT-EXAFS fitting curves of Pt@In. **Fig. S8.** The polarization curves with 85% iR compensation. **Fig. S9.** Time-dependent current density curves of In, Pt@In and Pt/In. **Fig. S10.** Faradaic efficiencies of formate, H₂ and CO over In, Pt@In and Pt/In. **Fig. S11.** Durability via i-t-test of Pt@In in the H-cell configuration for 50 h at −1.1 V. **Fig. S12.** XRD pattern of Pt@In on carbon paper after durability test. **Fig. S13.** Nyquist plots of In, Pt@In and Pt/In. **Fig. S14.** CV curves of (a) In, (b) Pt@In, (c) Pt/In, (d) double-layer capacitances (C_{dl}) of above materials. **Fig. S15.** ECSA normalized partial current densities for formate of prepared catalysts. **Fig. S16.** Effect of pH on CO₂RR performance over In and Pt@In. **Fig. S17.** I-t curves of different catalysts at −1.1 V in a CO₂-saturated 0.5 m KHCO₃ solution with 0.1 M t-BuOH. **Fig. S18.** XRD pattern of different catalysts on carbon paper after trapping test. **Fig. S19.** Changes in the visible light absorption properties of In and Pt@In after activation with temperature. **Fig. S20.** Work function of In, Pt@In and Pt/In. **Fig. S21.** Adsorption of OH⁻ as a surrogate for CO₂⁻. Oxidative LSV scans of In, Pt@In and Pt/In measured in Ar saturated 0.1 M KOH electrolyte. **Table S1.** Pt contents of Pt@In and Pt/In determined by ICP. **Table S2.** In contents of In, Pt@In, and Pt/In determined by ICP. **Table S3.** The relative ratio of oxygen vacancies to lattice oxygen. **Table S4.** Performance comparison of previously reported In-based catalysts for CO₂RR to formate. Supplementary data to this article can be found online at <https://doi.org/10.1016/j.cej.2026.179458>.

Data availability

Data will be made available on request.

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