

Electrochemical Production of Formic Acid from CO₂ with Cetyltrimethylammonium Bromide-Assisted Copper-Based Catalysts

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The electrochemical reduction of CO_2 (ERC) to valuable chemicals has attracted extensive attention. However, the relatively low selectivity and efficiency of the reaction remain challenges. In this study, Cu electrodes derived from Cu₂O with predominant (111) facets are synthesized by cetyltrimeth-ylammonium bromide-assisted preparation. The optimized electrode shows a high faradaic efficiency of 90% for HCOOH obtained by ERC at -2.0 V (vs.SCE), which surpasses most reported Cu electrodes. Based on a comprehensive analysis of

Introduction

In recent decades, a continuous increase of CO_2 emissions into the atmosphere has become a major contributor to the greenhouse effect. The conversion of CO_2 into valuable products from renewable energy is a potential way to mitigate the negative effect. Among various CO_2 conversion techniques, the electrochemical reduction of CO_2 (ERC) is regarded as one of the most attractive strategies. However, the ERC suffers from serious kinetic barriers, intricate multistep reactions and competing hydrogen evolution reaction (HER), leading to high overpotential, low conversion rate and poor product selectivity for the reaction.

Among different products generated from ERC reaction, HCOOH is quite appealing due to its excellent characteristics of nontoxicity, safety and transportability,^[1] which is also promising for hydrogen storage and fuel cells. To date, Pb, Pd, Sn, In, Co, Bi and SnO₂ electrodes have been successfully employed to convert CO₂ to HCOOH with high faradaic efficiency (FE) of over 90%.^[2] Among the reported metals, it is worth to mention that copper has been widely explored as an electrocatalyst for ERC due to its appropriate binding strength to ERC intermediates and diversified products. The desired product yielding can be

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the relationship between the catalytic activity and the thickness of the Cu₂O layer, the catalytic activity of the unit active site on the Cu₂O-derived Cu electrodes is found to be higher than that on the blank Cu electrode. DFT calculations indicate that OCHO* would be produced preferentially over *COOH in the presence of cetyltrimethylammonium bromide (CTAB). This deduction is verified by testing of the effects of CTAB and KBr addition on HCOO⁻ selectivity.

tuned by the Cu surface modification or its crystal structure regulation.^[3] More recently, sulfur-doped copper catalyst has been reported to produce HCOOH as an almost exclusive ERC product.^[4] Copper oxides have also been reported as electrocatalysts for conversion of CO₂ into HCOOH with moderate selectivity (ca. 59%) and activity.^[5] Since ERC reaction occurs on the interface of the electrode and the electrolyte, some specific chemicals presenting in the electrolyte might alter the binding energy of the key intermediates through adsorbing on the electrode surface, leading to the change of the ERC activity and product selectivity.^[6] For example, Cu electrodes modified with amino acid have exhibited noticeably improved hydrocarbon productivity and selectivity.^[7] In addition, adsorbed halide anions on the Cu surface have been confirmed to be able to facilitate the electron transfer at the interface by guickly stabilizing the adsorbed ERC intermediates.^[8]

In this study, Cu₂O layer was synthesized on copper substrate by a hydrothermal method and cetyltrimethylammonium bromide (CTAB) was used to modulate the morphology and the effective active sites of the copper electrode. CTAB is selected since Br⁻ has been regarded as an efficient capping agent to manipulate the facet exposure^[9] and the large cation (CTA⁺) has the ability to absorb on the substrate surface to tune the crystal growth.^[10] Enhanced HCOOH formation is obtained with the faradaic efficiency as high as 90% under -2.0 V (vs. SCE), which is the highest value based on copper electrodes. As a comparison of morphology regulator, KBr was also used in the hydrothermal reaction to explore the specific adsorption effect of Br⁻ on HCOOH formation. Cu-based electrodes prepared in the basic precursor without any additions and with different amounts of KBr or CTAB are designated as Cu–Blank, Cu–KBr(x), and Cu–CTAB(x), respectively, where x mmol is the additive concentration.



Results and Discussion

Composition and morphology of the Cu_xO electrodes

X-ray diffractogram reveals that Cu₂O was successfully generated on the electrodes (Figure 1a). The distinctly weakened diffraction intensity of the Cu(111) and Cu(200) observed for the underlying Cu sheet (see the Supporting Information, Figure S1) implies that the obtained Cu₂O layer on Cu-Blank is much thicker than the other two electrodes. According to the electrode order of Cu–Blank, Cu–KBr(2) and Cu–CTAB(2), the intensity ratios $I_{Cu_2O(111)}/I_{Cu_2O(220)}$ are 0.72, 0.81, and 1.57, respectively, indicating that CTAB incorporation is conducive to the priority generation of Cu₂O(111). This is due to the contribution of Br⁻ capping effect, which can absorb on Cu₂O(111) facet to retard its growth rate.^[9b,10a]

SEM images show that electrode morphology can change with different amounts of added CTAB (Figure 1b–g). A Cu₂O layer with dark red color can be observed on the Cu–Blank, and the surface is composed of polyhedral particles (size > 1.5 µm) with well-defined boundaries (Figure 1b). After adding CTAB into the basic precursor, the surface color gradually approaches the intrinsic color of Cu₂O (brick red), and the boundaries of the crystal facets are smoother with pits or bumps appearing on specific facets (Figure 1c–f). With higher CTAB concentration, particles with discontinuous rough surfaces (pits smaller than 100 nm) can be observed (Figure 1e,f), which finally evolves to be continuous with a size of small particles less than 100 nm. The rough surface and small particles are expected to extend the surface area and improve the reaction rate.

Catalytic activity and product selectivity

The thickness of the Cu_xO layer can be estimated based on the time span required to reduce Cu_xO under a specific reduction potential.^[2j] For Cu–CTAB(2), about 1600 s is required before a stable current is obtained (Figure S2a), whereas the time for Cu-Blank is more than 3000 s, indicating a much thinner Cu_xO layer

obtained on Cu-CTAB(2), and the result keeps consistent with XRD results. On the other hand, the decreased reduction current on the Cu-CTAB(2) (15 mA vs. 18 mA on the Cu-Blank) implies the active site number on Cu-CTAB(2) is smaller than that on Cu-Blank. Furthermore, compared with the Cu-Blank, the dynamic current has been increased by 71% on Cu-CTAB (2) under -1.9 V (vs. SCE; Figure S2b), suggesting the catalytic activity of Cu-CTAB(2) has been greatly improved. H₂-TPR testing results (Figure S2c and Table S1) demonstrated that the peak area of H_2 reduction for the three electrodes is: $S_{Cu-Blank} >$ $S_{Cu-KBr(2)} > S_{Cu-CTAB(2)}$, implying that the number of the active sites sequence for the three electrodes also follow the same rules. On the other hand, the H₂-TPR spectra are deconvoluted to identify the Cu_xO species on the three electrodes (Figure S3). The deconvolution results demonstrate the almost unique composition of Cu₂O on Cu-CTAB(2), whereas trace amounts of CuBr and CuO might be present on Cu-KBr(2) and Cu-Blank, respectively. SEM observations confirm the thickness estimation of the three electrodes with electrochemical spans (Figure S4), in which the Cu_xO thickness sequences on the substrate is: $\delta_{Cu-Blank} > \delta_{Cu-KBr(2)} > \delta_{Cu-CTAB(2)}$. The Cu_xO layer on the surface of the Cu-Blank electrode is relatively loose, whereas that on the surface of Cu-CTAB (2) electrode is thin and dense. Considering the thinner Cu_xO layer and lower number of active sites on Cu-CTAB(2), it can be readily inferred that the catalytic activity of the unit active site on the Cu electrodes with CTAB-assisted preparation has been improved.

The distribution of the catalytic products on the Cu_xOderived electrodes for ERC reaction has been distinctly different from that on the underlying Cu sheet (Figure 2 and Figure S5). On the sample of Cu–Blank (Figure 2a), diversified products distribution can be observed with a maximum FE_{HCOOH} of 40% at -1.7 V, which is close to the reported results.^[11] Conversely, the FE_{HCOOH} is up to 90% under -2.0 V for Cu–CTAB(2) (Figure 2b), which is more than 2 times of that on the Cu–Blank and has surpassed most of the reported Cu-based electrodes (Table S2). The high selectivity for HCOOH can be mainly attributed to the developed Cu₂O-derived layer on the Cu electrode, as the addition of CTAB can only contribute less than



Figure 1. Crystal structure (a) and the particle morphology as well as the surface appearance (b–g) of the prepared materials: b) Cu–Blank; c) Cu–CTAB(0.5); d) Cu–CTAB(1); e) Cu–CTAB(2); f) Cu–CTAB(4); g) Cu–KBr(2).





Figure 2. Faradaic efficiency of ERC products on Cu–Blank (a), Cu–CTAB(2) (b), TGP-H-060 (c), and Cu–KBr(2) (d) under different applied potentials. For (c), 0.5 mM CTAB was added into 0.2 M NaHCO₃ solution.

10% FE for the HCOOH production (Figure 2c). Furthermore, the Cu surface is negatively charged during the ERC process, which is favor to the competitive adsorption of the large cation (CTA⁺) on Cu active sites, as a result, active sites for H* adsorption is decreased and the H* coverage is reduced. The inhibited H₂ generation on Cu–CTAB(2) confirms the above assumptions.

In addition, hydrocarbons were not detected on Cu–CTAB (2), indicating a relatively simple product composition. Based on the comparison, it can be speculated that the pure Cu₂O phase prepared by the CTAB-assisted hydrothermal reaction is beneficial to selectivity towards HCOOH as the main product of the ERC reaction.

The thickness of the prepared Cu_xO layer gradually decreases with increasing CTAB concentration, which can be expressed by the time span required to reduce the Cu_xO layer, which is more than 3000 s for the Cu–Blank and less than 600 s for Cu–CTAB(4) (Figure 3a). The activity of the Cu–CTAB electrodes demonstrates a non-monotonic variation trend (Figure 3b). The optimum content of CTAB in the hydrothermal precursor is 2 mM. Under -1.75 V (vs. SCE), the produced HCOOH concentration on the Cu–CTAB(2) is 300% more than that on Cu–Blank with a high FE_{HCOOH} of 80% (Figure 3c,d). This selectivity variation trend implies that CTAB addition is capable of tuning the product distribution of Cu-based electrodes, which offers

great potential for extending the application of Cu-based catalysts.

Under all applied potentials, the liquid resistance of the Cu–CTAB (2) electrode is lower than that of the Cu–Blank electrode (Figure S6 and Table S3), which may be related to the residual CTAB on the surface. When the ERC reaction is performed at low overpotential, the charge transfer resistance (R_{ct}) of the Cu–CTAB(2) electrode is far lower than that of the Cu–Blank electrode, indicating a rapid kinetic reaction rate of ERC for the Cu–CTAB(2). At medium overpotential, the R_{ct} is essentially similar for all the electrodes. While mass transfer polarization of Cu–CTAB(2) electrode can be observed at higher overpotential, which may be attributed to the violent ERC reaction and insufficient supply of CO₂ concentration.

Study on the improvement mechanism of catalytic activity and selectivity toward HCOOH on Cu_xO electrode

To unveil the possible reasons behind the significant selectivity to HCOOH on Cu–CTAB electrodes, the composition in the electrolyte after ERC reaction is analyzed by ion chromatography and the surface functional groups are detected through FTIR. Br^- is detected in the electrolyte after ERC reaction (Table 1), indicating a trace amount of residual CTAB on the Cu–CTAB electrode surface. FTIR spectroscopy further confirms



Figure 3. Effect of CTAB addition on Cu_xO layer thickness (a), activity (b), HCOOH concentration (c) and product selectivity (d) of ERC reaction catalyzed by Cu_xO-derived electrodes.

Table 1. Br detection by ICS-1100.			
Precursor	$C_{\rm Br}^{-}$ [ppm] in 0.2 M NaHCO ₃ (aq)		
0.2 M NaHCO₃ (aq)	_		
Cu–Blank	-		
Cu–CTAB(0.5)	0.2		
Cu–CTAB(1)	0.2		
Cu–CTAB(2)	12		
Cu–CTAB(4)	18		

this assertion (Figure 4a). Energy-dispersive X-ray spectroscopy (EDX) results also show CTAB retention on the Cu–CTAB surfaces (Figure S7 and Table S4). The mass spectrometry test of H₂–TPR effluent (Figure S8) demonstrate that the Cu–CTAB(2) electrode produces CO_2 when the temperature is lower than 220 °C, which can be caused by the thermal decomposition of CTAB remaining on the electrode surface (the thermal decomposition temperature of CTAB is ca. 150 °C). The MS results further indicate that organic species exist on the surface of Cu–CTAB(2) electrode.

Based on the detected CTAB on the Cu–CTAB electrodes, one can firstly doubt whether the improved selectivity of HCOOH on the Cu–CTAB electrode is ascribed to the specific adsorption of Br⁻. The second question is whether the residual CTAB has a coverage effect over the active sites on the surface of the Cu–CTAB electrodes. The selectivity improvement of HCOOH on the referenced Cu–KBr(2) electrode can partially answer the first query. A thinner layer and a much higher reduction current are obtained on Cu-KBr(2) than on Cu < C-Blank (Figure S2a,b), indicating the specific adsorption of Brcan significantly increase the catalytic activity of the Cu_xOderived electrodes. HER is significantly inhibited with the lowest FE_{H2} close to 20% on Cu–KBr(2) (Figure 2d). However, the ERC products are diversified and the best selectivity to HCOOH occurs at -1.75 V with a FE of 63%. Significant amounts of CO can also be detected with FE from 20% to 40%, which is partially attributed to the impure Cu₂O phase (small amount of CuBr; Figure 1a and Figure S3c). The results suggest that the specific adsorption of Br⁻ on the Cu_xO electrode surface can alleviate the occurrence of the competitive HER, but the ERC products, especially HCOOH, were not selectively formed as the most preferable component. In addition, the well-defined morphology of Cu-KBr(2), which is totally different from those of the Cu–CTAB(x) electrodes (Figure 1f), further confirms that specific adsorption of Br⁻ did not change the Cu_xO growth mechanism. Therefore, the steric hindrance effect of CTAB might be the main reason for the growth of smooth particles and the crystal orientation of the Cu_xO layer.^[10] In addition, the surface composition of the Cu-CTAB(2) electrode after the ERC reaction is different from the other two electrodes (Figure S9). The $I_{Cu(111)}/I_{Cu(200)}$ ratio is close to 1, whereas the value is much higher for the other two electrodes. These results reflect that the surface composition of the Cu-CTAB (2) electrode is predominantly Cu(110) after potential reduction.





Figure 4. a) FTIR spectroscopic detection of additives on Cu_xO-derived electrodes. b) Validation of the beneficial effect of CTAB on ERC product selectivity. The working electrode is Cu–Blank. c) Tafel slope comparison of Cu_xO electrode-catalyzed ERC reactions. d) Electrochemical measurement of surface roughness for Cu–CTAB(2) and Cu–Blank.

To answer the second question, i.e., whether the CTAB coverage on the surface of Cu–CTAB electrodes can affect the catalytic properties of the active sites, 0.5 mM CTAB was directly added to 0.2 M NaHCO₃ aqueous solution, and the variations of FE for each product are shown in Figure 4b. By comparison of the curves in Figures 4b and 2b, it can be easily deduced that the variation trends of the three products (CO, HCOOH, and H₂) are very similar. Especially, the tendency is almost the same when the potential is lower than -1.4 V (vs. SCE), suggesting that CTAB addition into the electrolyte can significantly improve HCOOH selectivity along with the distinct inhibition of the HER.^[12]

This result implies that the selectivity of HCOOH can be significantly improved by simply covering CTAB on the surface of Cu–Blank electrode. On the other side, CTAB might cover on those active sites favoring the competitive HER when comparing the FE_{H₂} values in Figure 2a and 4b. As CTAB addition in the basic precursor is beneficial to the generation of Cu₂O(111) (Figure 1a), we can reasonably deduce the improved HCOOH selectivity to the Cu₂O(111) preference. Considering the ERC intermediates, it is speculated that Cu₂O(111)-derived Cu facet might facilitate the first proton-electron transfer of the ERC reaction, and reduce the energy barrier from CO₂ to OCHO^{*-} (HCOO^{*-}). Tafel slope testing confirmed the above assumption (Figure 4c). A Tafel slope of 152 mV dec⁻¹ is obtained with

Cu–CTAB(2) catalyzing the ERC reaction, which is 17% lower than that on the Cu–Blank. This means the electrochemical resistance of the ERC reaction has been decreased, which is consistent with the catalytic activity improvement of the unit active site.

Another probability leading to the smaller electrochemical resistance might be a rougher surface on the prepared Cu–CTAB layer than that of the Cu–Blank, thus extending the electrochemical reaction areas. However, the lower surface roughness of the Cu–CTAB (2) than that of the Cu–blank (Figure 4d and Table S5) and the lower surface active sites (Figure S2c) seem to be deviated from the expectation. The smaller surface area participating in the ERC reaction on the Cu–CTAB and the higher catalytic activity (Figure S2b) confirms once more the catalytic activity of the unit active site on Cu–CTAB(2) is higher than that on Cu–Blank.

DFT calculations on the role of CTAB involvement at the electrode-electrolyte interface

Interfacial properties at the boundary between the electrode and electrolyte have important effects on the surface reactivity in electrocatalysis. To fairly reveal the role of CTAB involvement at the electrode-electrolyte interface, an in-depth thermody-



namic analysis on top of DFT calculation has been carried out. By concentrating on Cu₂O-derived Cu(110) surface, we investigate the Gibbs free energy diagram along two established reaction pathways proposed in related literatures of ERC on Cu(110) surface with and without CTAB involvement (Figure 5 and Table S6).^[13] In addition, both more stabilized *COOH and OCHO* intermediates rationalize the overall increment of the unit active site in the presence of CTAB, despite the lower surface roughness. On other hand, the Gibbs free energy of the elementary reaction $CO_2^* \rightarrow OCHO^*$ is lowered by 0.34 eV (from -0.42 eV to -0.76 eV), while the value of $CO_2^* \rightarrow ^*COOH$ was lowered by only 0.2 eV, indicating OCHO* would be yielded preferentially over *COOH resulting in higher selectivity of HCOOH. The more negative potential further promotes this preferential more obviously (Figure S10). The decreased FE_{co} in Figure 2b is consistent with the DFT calculation results.

Stability of the Cu-CTAB electrode during ERC reaction

It is well known that the Cu electrodes are less stable in the prolonged ERC reaction.^[14] To examine the stability of the HCOOH selectivity catalyzed by the Cu–CTAB electrode, a nearly 8 h durability test was conducted (Figure S11). The reaction current reaches its maximum within 1 h and then gradually decreases. At the end of the reaction, the current decrement is ca.11% while the FE_{HCOOH} exhibits ca. 16% reduction (from 87% to 73%), implying an excellent stability for ERC reaction and the superior catalytic activity maintenance. The SEM observations (Figure S11c,d) reveal that slight morphology changes have been occurred which has not detrimental influence on the high selectivity of HCOOH.

Conclusions

In summary, a facile method to prepare oxide-derived (OD) Cu electrodes was developed by using a CTAB-assisted strategy during the hydrothermal reaction process, which can afford pure Cu_2O phase with (111) preference. The prepared Cu

electrodes showed high selectivity toward HCOOH. The electrode synthesized with 2 mM CTAB addition exhibited the highest FE_{HCOOH} of 90%, which is approximately twice that on the Cu-Blank electrode and surpasses most reported Cu-based electrodes. The Cu-CTAB(2) electrode maintained approximately 80% of its initial faradaic efficiency(FE_{HCOOH}) over 8 h, showing excellent stability for the ERC reaction. In comparison of the activity, the thickness of Cu_xO layer, and HCOOH concentrations, the unit active site on the Cu-CTAB electrode derived from Cu₂O, which was produced by the CTAB-assisted hydrothermal method, was deduced to have higher catalytic activity than the Cu-Blank electrode. By combining experimental verification of the effects of CTAB and KBr addition on HCOOH selectivity with DFT calculations, we deduce that competitive CTA⁺ adsorption on the active sites, which inhibits H₂ formation, and the pure Cu₂O phase with predominant Cu₂O(111) orientation reduce the energy barrier from CO₂ to OCHO*, which contributes to the high selectivity to HCOOH on the Cu-CTAB electrode. These findings provide mechanistic insight into an earth-abundant ERC catalyst, and we expect that the selectivity toward HCOOH can be further enhanced on Cu–CTAB electrodes by increasing the CO₂ concentration in the electrolyte.

Experimental Section

Preparation of the Cu_xO-derived electrodes

1 mM of CuAc₂ (Aladdin Industrial Corp., 99.5%) aqueous solution was used as the basic precursor of the hydrothermal reaction. Cu_xO electrodes were prepared with or without the addition of KBr or CTAB under the hydrothermal environment. For the additive-assisted hydrothermal reactions, KBr or CTAB powder (Aladdin Industrial Corp., 99.0%) was firstly introduced into the basic precursor solution under vigorous stirring to obtain the Cu precursor of the hydrothermal reaction. The KBr concentration is controlled as 2 mM, and that of CTAB is 0.5 mM, 1 mM, 2 mM and 4 mM, respectively. Then, 60 mL Cu precursor solution and Cu sheet (99.7 wt%) were transferred into a 100 mL Teflon-lined stainless-steel autoclave. The autoclave was treated under 180°C for 12 h and then cooled down naturally. Thirdly, the Cu sheet covered with Cu_xO layer was taken out from the autoclave, rinsed thoroughly



Figure 5. Free energy diagrams of ERC on the surface of Clean_Cu (a) and CTAB_Cu (b).



with ultrapure water and dried under Ar atmosphere. Finally, the electrode was electrochemically reduced in CO_2 -bubbled 0.2 M NaHCO₃ at -0.9 V (vs. SCE) for 2 h to obtain the Cu_xO-derived Cu electrode. Cu-based electrodes prepared in the basic precursor without any additions, and with different amount of KBr or CTAB are designated as Cu–Blank, Cu–KBr(x), Cu–CTAB(x), respectively, where x represents the additive concentration.

Surface roughness determination

Electrochemical cyclic voltammetry was employed to test the double layer charging capacitance of Cu_xO electrode to characterize the electrochemical reaction surface area participating in the ERC reaction. The test solution is N₂ saturated 0.1 M HClO₄ and the potential window is -0.24 V to -0.34 V(vs. SCE).

Characterization

Powder X-ray diffraction (XRD) spectra were measured on a Rigaku Ultima IV diffractometer with $Cu_{k\alpha}$ radiation (l=0.15418 nm) operating at 40 kV and 40 mA over the two theta range of 5–100° with a scan speed of 10° min⁻¹. Scanning electron microscopy (SEM) was recorded on JEOL JSM-6360 operating at an acceleration voltage of 20 kV. Br element quantities were detected by EDX. The IR spectra were recorded with a Fourier Transform Infra spectrometer (Nicolet iS50, Thermo Fisher, USA) in the 2000–400 cm⁻¹ wavenumber region with ATR technique. H₂–TPR was carried out on Micromeritics Chemi 2920 II. 10%H₂/90%Ar stream with flow rate of 30 mLmin⁻¹ was used to determine the Cu_xO species and the number of the surface active sites, the temperature rise rate of 10°Cmin⁻¹. The effluent of the H₂–TPR was detected by the MS (MKS104-J0316005) to detect the reduction product.

Electrochemical testing

The Electrochemical measurements were performed on a potentiostat (EG&G 2273, Princeton Applied Research) in a self-made H cell (separated by Nafion115). Pt sheet and saturated calomel electrode (SCE) were used as the counter electrode and the reference electrode, respectively. The prepared Cu-based electrode was used as the working electrode. CO₂-saturated 0.2 M NaHCO₃ aqueous solution was used as the electrolyte. The generated gas products were analyzed online by a gas chromatograph (GC, Shimadzu GC-2014).The hydrogen and CO were quantified by a thermal conductivity detector (TCD), and hydrocarbons were detected and quantified by flame ionization detector (FID), respectively. The liquid products including Br⁻ were quantified by ion chromatography (ICS-1100, Dionex Corporation).

Computational details

All DFT calculations were performed with the Quantum ESPRESSO code^[15] employing the state-of-art Bayesian error estimation functional with van der Waals correlation (BEEF-vdW),^[16] which has been successfully used for surface chemistry studies. We used soft pseudopotentials and a vacuum region of 30 Å perpendicular to the surface. Pseudopotentials for C, O, H, Cu, and N were generated by using the "atomic" code reported by Dal Corso (v.5.0.2 svn rev. 9415).^[17] In terms of our experimental observation, Cu₂O-derived the typical (110) facet of Cu with and without CTAB involvement was modeled using periodic slabs, where (3×3) unit cell and 4 layers were used. The bottom-most layer was fixed in their bulk truncated positions, while the layers above were relaxed until reaching a maximum force threshold of 0.03 eV/Å. k-point sampling

was carried out using (4×4) grid. The cutoff energy was set to 500 eV and 5000 eV for the orbitals, and the charge density, respectively, and a Fermi level smearing of 0.1 eV was used. Spin polarization and dipole correction have been involved for all the calculations. To ensure computationally tractable, we use a simplified model of CTAB, C6H16N, with a shorter carbon chain considered since the carbon chain has a negligible influence on the ERC reaction. Potential asymmetric adsorption sites of each intermediate were calculated and only the most favorable was used.

The Gibbs free energies of typical proton-coupled electron transfer steps are estimated using the CHE approach,^[18] where the free energy of the solvated proton and electron pair can be by definition equal to one-half the chemical potential of molecular H₂ at 101325 Pa, further as a function of applied potential at all temperature and PH values. Within the CHE approach, the free energy of intermediate is calculated by $G = E + ZPE - T\Delta S$, in which *E* is the DFT-optimized total energy, ZPE is the zero-point vibrational energy, *T* is the absolute temperature, and ΔS is the entropy change. For the adsorbed intermediates, the ZPE and entropy were calculated using the harmonic approximation with the ASE module vibrations.^[19] The value of entropy of gas phase was taken from NIST,^[20] while the ZPE of gas phase were also obtained from vibrational frequencies from ASE.

To simulate the chemical reaction in electrocatalysis, the effect of solvent stabilization should be taken into account for adsorbed species, as well as gas-phase error corrections for the standard free energy deduced from the limitation of exchange-correlation functional. It is noticed that the gas-phase error corrections are functional dependence (BEEF-vdW functional in our case), where the values are taken from reference [21], in which they implement systematic investigation gas-phase error on few various exchange-correlation functional used prevalently (PBE, PW91, RPBE, and BEEF-vdW). Regarding the independent solvation correction of adsorbed species involved in ERC, we use the result of previous work obtained from the sensitivity analysis, which is 0 eV, -0.1 eV, -0.25 eV for OCHO*, *CO and *COOH.^[22]

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Conflict of Interest

The authors declare no conflict of interest.

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