Tracking structural evolution: \textit{operando} regenerative CeO$_x$/Bi interface structure for high-performance CO$_2$ electroreduction

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ABSTRACT

Unveiling the structural evolution and working mechanism of catalysts under realistic operating conditions is crucial for the design of efficient electrocatalysts for CO$_2$ electroreduction, yet remains highly challenging. Here, by virtue of \textit{operando} structural measurements at multiscale levels, it is identified under CO$_2$ electroreduction conditions that an as-prepared CeO$_2$/BiOCl precatalyst gradually evolves into CeO$_x$/Bi interface structure with enriched Ce$^{3+}$ species, which serves as the real catalytically active phase. The derived CeO$_x$/Bi interface structure compared to pure Bi counterpart delivers substantially enhanced performance with a formate Faradaic efficiency approaching 90% for 24 hours in a wide potential window. The formate Faradaic efficiency can be further increased by using isotope D$_2$O instead of H$_2$O. Density functional theory calculations suggest that the regenerative CeO$_x$/Bi interfacial sites cannot only promote water activation to increase local $^*$H species for CO$_2$ protonation appropriately, but also stabilize the key intermediate $^*$OCHO in formate pathway.

Keywords: CO$_2$ electroreduction, electrocatalyst, nanosheet, structural evolution, interface

INTRODUCTION

Recent years have witnessed explosive development in electrochemical CO$_2$ reduction into valuable chemicals or fuels [1–5]. CO$_2$ electroreduction is considered as a promising route to utilizing renewable electricity [6,7]. Designing high-performance electrocatalysts is pivotal to tuning CO$_2$ activation, thus achieving the highly selective CO$_2$ conversion into target products [8–10]. However, the rational design of electrocatalysts faces severe challenges, because most of the catalysts would go through dynamic structural evolution under applied electric field [1,6,11–13]. The ambiguous evolution rules also hinder the uncovering of the working mechanism. Generally, the real catalytically active phase is inconsistent with the as-prepared or post-catalyzed catalyst structure. The established structure–performance relationship based on \textit{ex situ} static characterizations does not match the realistic catalytic phenomenon. For instance, positive-valence metal species would be electrochemically transformed into so-called zero-valent metals during CO$_2$ electroreduction [6,7,14]. In this regard, some studies pointed out that the presence of slight positive-valence metal species in the derived structure is the key to realizing highly efficient CO$_2$ electrocatalysis [15–17]. More importantly, the evolution processes are closely related to the precatalytic structure and electrocatalytic conditions, including potentials, electrolytes, temperature, etc [11,12]. Nevertheless, it is not clear how the catalyst structure evolves, and how a real catalytically active component catalyzes CO$_2$ conversion under the corresponding environmental conditions [18]. To tackle the problems, \textit{in situ}/\textit{operando} characterization techniques, such as \textit{operando} Raman and X-ray absorption fine structure (XAFS) measurements, are solid methods to track
structural change, identify real active phases and uncover the underlying mechanism, thus guiding the structure design of highly active and robust catalysts [19–22].

Herein, we operando probed the structural evolution of as-prepared BiOCl nanosheets loaded with CeO$_2$ (denoted as CeO$_2$/BiOCl), which was obviously different from ex situ static characterizations either before or after a reaction. It has been found that the CeO$_2$/BiOCl precatalyst gradually evolved into a stable CeO$_x$/Bi interface structure with increased Ce$^{3+}$ species, under cathodic reduction potential with a certain strength (Fig. 1). The structural regeneration was attributed to their reversible reduction processes of Bi$^{3+}$ and Ce$^{4+}$ cations. Especially, the presence of CeO$_2$ component could facilitate the regeneration process, as evidenced by operando Raman results. The derived CeO$_x$/Bi interface structure (named as D-CeO$_x$/Bi) enabled highly selective and stable CO$_2$ electroreduction to formate, significantly outperforming the Bi and CeO$_x$ (denoted as D-Bi and D-CeO$_x$) counterparts derived from cathodic reduction of BiOCl and CeO$_2$. D$_2$O isotope labeling experiments have also been performed to probe the working mechanism, verifying that hydrogen source of formate product originated from water activation. Based on the operando structural identifications, the structure model for the regenerated Bi/CeO$_x$ interface structure was established. The computed Gibbs free energies of the reaction species indicated that the formation of key intermediate $^*$OCHO for formate pathway could be boosted at the regenerative CeO$_x$/Bi interfacial sites, thereby rationalizing the high selectivity experimentally.

RESULTS AND DISCUSSION

The BiOCl and CeO$_2$/BiOCl were obtained via a propylene oxide-assisted hydrolytic process, followed by thermal treatment at 400°C in air (see details in Methods). X-ray diffraction (XRD) measurements clarified that both BiOCl and CeO$_2$ components existed in the CeO$_2$/BiOCl (Supplementary Fig. 1). The CeO$_2$ nanoparticles (NP) were loaded onto typical BiOCl nanosheets to form interfacial structure, as confirmed by transmission electron microscopy (TEM) and corresponding fast Fourier Transform images (Fig. 2a and b, Supplementary Figs 2–4). Subjected to a cathodic reduction at $\sim$1.0 V versus reversible hydrogen electrode (RHE) for 30 minutes in CO$_2$-saturated 0.5 M KHCO$_3$ solution, slight structure change was observed for the D-CeO$_x$/Bi (Fig. 2c), probably due to the irreversible reduction of Bi$^{3+}$ and Ce$^{4+}$ cations [6,7,14]. The NP-loaded interfacial structure was maintained (Fig. 2d). As shown in Supplementary Fig. 5, the lattice spacing of 0.33 and 0.27 nm in the D-CeO$_x$/Bi were attributed to the Bi (012) and CeO$_2$ (110) planes (JCPDS No. 44-1246: Bi; JCPDS No. 34-0394: CeO$_2$), respectively [6,23,24]. The results indicated that the BiOCl was converted into metallic Bi, and the CeO$_2$ was apparently unchanged. We also identified that the two phases kept close interfacial contact from high angle annular dark field scanning TEM (HAADF-STEM) and the corresponding energy-dispersive X-ray (EDX) elemental mapping (Fig. 2e). Furthermore, the transformation process was also evidenced by X-ray photoelectron spectroscopy (XPS) results. The peaks of 164.8 and 159.5 eV corresponding to Bi$^{3+}$ species disappeared (Fig. 2f), and two new peaks at 163.9 and 158.6 eV ascribed to metallic Bi$^0$ were detected after the reduction process [14]. The Ce species kept typical signal peaks corresponding to Ce$^{3+}$ and Ce$^{4+}$ species both before and after the reduction (Fig. 2g). It is noted that the Ce$^{3+}$ species were obviously enriched from 26.1% to 42.3% as a result of the increase of oxygen defects during the reduction process (Supplementary Table 1) [24]. And these oxygen defects were readily filled by the hydroxyl in aqueous solution [25].
Figure 2. **Ex situ** static characterizations before and after the reaction. (a) TEM and (b) HRTEM images of the CeO$_2$/BiOCl. (c) TEM image, (d) HRTEM image and (e) the corresponding EDX elemental mapping of the D-CeO$_x$/Bi. (f) Bi 4f and (g) Ce 3d XPS spectra of the CeO$_2$/BiOCl and D-CeO$_x$/Bi.

As shown in Supplementary Fig. 6, for the CeO$_x$ sample, the peak at 1168 cm$^{-1}$ corresponded to the second-order longitudinal optical (2LO) mode of fluorite phase [26]. As to D-CeO$_x$/Bi, the peaks at 75 and 103 cm$^{-1}$ corresponded to typical vibration signal of metallic Bi [27]. Compared to that of CeO$_x$ sample, a new peak at 1071 cm$^{-1}$ emerged for the D-CeO$_x$/Bi, which was ascribed to the formation of Bi-O-Ce bonds [28,29]. The Raman results also indicated that Bi$^{3+}$ of BiOCl was reduced to Bi$^0$ species, and Bi/CeO$_x$ interfaces existed in the D-CeO$_x$/Bi. The standard electrode potential of $E^0$ (Bi$^{3+}$/Bi$^0$) is 0.308 V versus RHE [30], much more positive than the cathodic reduction potential of $-1.0$ V versus RHE. Therefore, the BiOCl was readily converted into metallic Bi. The $E^0$ (Ce$^{3+}$/Ce$^0$) is $-2.336$ V versus RHE, and $E^0$ (CeO$_2$/Ce$^{3+}$) is 1.4 V versus RHE. Thus Ce$^{4+}$ species in the CeO$_2$ component were readily reduced to the Ce$^{3+}$ species, but were hardly converted to Ce$^0$ species. It has to be pointed out that nanostructured metallic Bi is air-sensitive, and is easily surface-oxidized [24]. And the CeO$_2$ has the high ability to capture and release oxygen [31,32]. Therefore, combined with the above **ex situ** static characterizations, **in situ**/**operando** structural measurements have to be employed to identify the real active components accurately.

We carried out **operando** characterization measurements at multiscale levels to track the structural evolution and obtain dynamic structural information of the catalysts in CO$_2$-saturated 0.5 M KHCO$_3$ solution. First **operando** XRD measurement was performed to identify the evolution of crystal structure. Typically, from the **operando** XRD patterns (Supplementary Fig. 7), it can be seen that the peak of about $2\theta = 25.9^\circ$ corresponded to the (101) plane of BiOCl. When the cathodic reduction potential was increased to $-0.9$ V versus RHE, the peak disappeared. The new peak at about $2\theta = 27.2^\circ$ corresponding to the (012) plane of metallic Bi was emerged. The peak at about $2\theta = 26.6^\circ$ ascribed to carbon paper nearly remained unchanged. The signal from CeO$_2$ component was not detected in the **operando** test condition due to the relatively low content. The transformation of crystal structure was in accordance with the above TEM results. To achieve the identification of the dynamic geometric structure, we performed potential- and time-dependent **operando** Raman spectra (Fig. 3, Supplementary Figs 8 and 9). At open circuit potential (OCP), four typical Raman peaks at 67, 151, 207 and 405 cm$^{-1}$ were presented (Fig. 3), which were assigned to the A$_1g$ external Bi-Cl stretching mode, the A$_1g$ internal Bi-Cl stretching mode, the E$_g$ external Bi-Cl stretching mode and the external Bi-O stretching vibration in the BiOCl structure, respectively [33,34]. The peak at 461 cm$^{-1}$ corresponded to the F$_{2g}$ mode of Ce-O- Ce symmetric stretching...
vibration in the CeO$_2$ structure [35]. With gradually increasing cathodic potential to $-0.7$ V versus RHE, the peaks ascribed to that of the BiOCl were in decline (Fig. 3a and b). Meanwhile, it was accompanied by two new characteristic peaks at 75 and 103 cm$^{-1}$, which were corresponding to typi- cal vibration signal of metallic Bi [27]. Also note that the peak ascribed to the F$_{2g}$ mode of Ce-O-Ce symmetric stretching vibration also remained almost un- changed until $-0.7$ V (Fig. 3c). The peak vanished at higher potentials. With the increase of oxygen defects and reduced Ce$^{3+}$ ions at higher potentials, the signature vibrational band would exhibit a reduced and widened model system [26,36], thus leading to the apparent disappearance of the peak at about 461 cm$^{-1}$. Furthermore, we also dissected operando Raman spectra from 950 to 1200 cm$^{-1}$ (Supplementary Fig. 8). The peak of about 1071 cm$^{-1}$ remained nearly unchanged under applied potential windows, manifesting in the persistence of the Bi/CeO$_x$ interface throughout electrochemical tests. Additionally, by analyzing time-dependent operando Raman spectra at $-0.9$ V versus RHE (Supplementary Fig. 9), it was also found that the CeO$_2$/BiOCl compared to the BiOCl exhibited faster transformation process, probably because the presence of the CeO$_2$ could facilitate water dissociation to increase local proton concentration for the BiOCl reduction [37]. To further gain the information for electronic properties, we employed operando X-ray absorption near edge structure (XANES) measurements. From the normalized XANES spectra and local enlargement at the Bi L$_3$-edge (Supplementary Fig. 10), it was found that the BiOCl subjected to the cathodic reduction current of 1 and 10 mA/cm$^2$ aligned well with the Bi foil, and the shift of absorption edge could not be observed, demonstrating the complete absence of positive-valence Bi species [6,14]. The normalized Ce L$_3$-edge XANES spectra (Supplementary Fig. 11) show that the Ce species of CeO$_2$/BiOCl was almost reduced to Ce$^{3+}$ under CO$_2$ electroreduction conditions [35]. The result is inconsistent with Ce 3d XPS results as a result of the high ability of oxygen capture for oxygen vacancy-rich CeO$_x$ in air [31,32]. These operando characterization results provided solid evidences for the structural regeneration of the as-prepared CeO$_2$/BiOCl precatalyst into the defect-enriched CeO$_x$/Bi interface structure under the actual CO$_2$ electroreduction condition.

The electrochemical performance was estimated in a two-compartment gas-tight H-type cell within 0.5 M KHCO$_3$ solution (see details in Methods). In order to accomplish the structural regeneration, first the as-prepared CeO$_2$/BiOCl and BiOCl loaded onto carbon paper were electrochemically treated for 30 minutes at $-0.9$ V versus RHE. The linear sweep voltammetry (LSV) curves (Supplementary Fig. 12) displayed that the current densities were remarkably increased in CO$_2$-saturated electrolyte in contrast to Ar-saturated electrolyte, indicating that both the D-CeO$_x$/Bi and D-Bi favored CO$_2$ reduction over hydrogen evolution reaction (HER). Through analyses of the products, the D-CeO$_2$/Bi with Bi/Ce ratio (3:1) exhibited the optimized performance, displaying the highest formate Faradaic efficiency ($\text{FE}_{\text{formate}}$) of 92.0% at $-0.9$ V versus RHE (Fig. 4a, Supplementary Figs 13 and 14). The corresponding formate partial current density reached 22.1 mA/cm$^2$ (Fig. 4b), which was nearly two times higher than that of the D-Bi (12.0 mA/cm$^2$). The electrocatalytic performance
Figure 4. Performance evaluation of CO₂ electroreduction. (a) Potential-dependent FE_{formate} of the D-Bi and D-CeOₓ/Bi. (b) Potential-dependent formate partial current density of the D-Bi and D-CeOₓ/Bi. (c) Long-term stability and selectivity of D-CeOₓ/Bi at −0.9 V versus RHE. (d) Potential-dependent formate partial current density of the D-CeOₓ/Bi under H₂O and D₂O conditions. (e) Potential-dependent FE_{formate} of the D-CeOₓ/Bi under H₂O and D₂O conditions. (f) ¹H nuclear magnetic resonance (NMR) spectra of the D-CeOₓ/Bi under H₂O and D₂O conditions.

of both D-Bi and D-CeOₓ/Bi is significantly better than of D-CeOₓ (Supplementary Fig. 15), evidencing the importance of Bi components on high formate selectivity [6,7,14]. The electrochemical surface area (ECSA)-normalized partial current density of D-CeOₓ/Bi was still 1.5 times larger than that of D-Bi (Supplementary Fig. 16), suggesting the key role of the interfacial structure on enhancing intrinsic activity [25,35]. We also identified that the FE of products that contain carbon element (formate and CO) maintained over 90% at a wide potential window of approximately −0.7 to −1.0 V (Supplementary Fig. 17). In addition to the good activity and selectivity, the D-CeOₓ/Bi also displayed long-term stability of formate production for 24 hours (Fig. 4c).

To probe the underlying mechanism of CO₂ electroreduction into formate onto the D-CeOₓ/Bi, we carried out in situ Fourier transformation infrared (FTIR) measurements and D₂O labeling experiments. As shown in Supplementary Fig. 18a, the broad band between 1350 and 1450 cm⁻¹ arose from the dissolved CO₃²⁻/HCO₃⁻ and formate [38–40]. The broad band gradually rose with increasing reduction potential, suggesting the accumulation of formate [38]. The reversed peak at about 1650 cm⁻¹ is attributed to the consumption of interfacial H₂O [41,42], implying the H₂O participation in the formate formation. Meanwhile, the doublet peak at about 2350 cm⁻¹ declined when the cathodic reduction potential or the electrolytic time was increased (Supplementary Fig. 18b and c), which are attributed to the consumption of gaseous CO₂ [43]. From potential-dependent current densities of the D-CeOₓ/Bi under H₂O and D₂O conditions (Fig. 4d, Supplementary Fig. 19), we could identify that the partial current densities of total formate (HCOO⁻ and DCOO⁻) under D₂O condition were lower than that under H₂O condition when the potential was between −0.6 and −1.0 V. For the potential window of −1.0 to −1.2 V, the partial current densities under D₂O condition were larger relative to that under H₂O condition. The FE formate under D₂O condition was always higher than that under H₂O condition under total measured potential window (Fig. 4e, Supplementary Fig. 20). The changed activity and selectivity meant that the formate formation was moderately promoted, and the hydrogen evolution was inhibited under D₂O condition. To disclose the reason, the HCOO⁻ content in the total electrolyte was determined by ¹H nuclear magnetic resonance (NMR) (Fig. 4f). Through analyzing the relative amount of HCOO⁻ and DCOO⁻ in the total formate (see details in Methods), it was uncovered that the DCOO⁻ content of 91.7% at −0.9 V was much greater than the HCOO⁻ content, which demonstrated that the hydrogen source of formate...
mainly came from water activation [44]. Therefore, it could be easily understood that the water activation under D2O condition was harder than that under H2O condition, causing the insufficient supply of absorbed *D species for the formate formation at low overpotentials. At high overpotentials, the supply of the absorbed *D species was sufficient. The appropriately inhibited water activation enabled less release of gaseous hydrogen, thus leading to the higher formate partial current densities and selectivity.

We further employed density functional theory (DFT) calculations to understand the enhanced reason of the regenerated Ce3+−enriched CeO2/Bi interface toward formate formation. Based on the above operando structural identifications, structure models for the Bi and CeO2/Bi surfaces as well as corresponding adsorption configurations of intermediates were rationally established (Fig. 5a and Supplementary Fig. 21). In the structure models, the Ce3+ species were considered as the Ce atoms that were bound with hydroxyls [25]. The formation of *OCHO and *COOH intermediate were demonstrated as the key of HCOOH and CO pathway, respectively [45,46]. For the HCOOH pathway, the Gibbs free energies for the formation of *OCHO onto Bi and CeO2/Bi surfaces were 0.48 and 0.20 eV, respectively (Fig. 5b). The introduction of CeO2 onto Bi surface efficiently stabilized the *OCHO through binding one O atom of *OCHO with the Ce atom (Supplementary Fig. 21c). On the other hand, the calculated Gibbs free energies for CO pathway onto both the Bi and CeO2/Bi surfaces were larger than that for HCOOH pathway (Fig. 5c), strongly supporting higher selectivity toward formate than that toward CO onto typical Bi-based materials. To understand the effect of CeO2/Bi interface on water activation, we also calculated the Gibbs free energies of HER onto Bi and CeO2/Bi surfaces (Fig. 5d). The Gibbs free energies for the *H formation onto the Bi surface were 0.92 eV. The value for the CeO2/Bi surface was remarkably decreased to 0.42 eV. The results indicated that water activation could be efficiently enhanced through introducing CeO2 components onto the Bi surface. In terms of the competition between HER and HCOOH formation, it could be identified that the formation energies of the key intermediate *OCHO were always lower than that of *H, theoretically interpreting the preferential HCOOH formation onto the CeO2/Bi interfacial structure, despite the boosted water activation. Combining these calculation results with the above isotope labeling evidences, it could be reasonably deduced that the water activation at the interfacial sites was properly improved to provide the *H species for the formation of the key intermediate *OCHO in HCOOH pathway, thus accounting for the increased selectivity of formate experimentally.

CONCLUSION

In summary, we have reported the tracking of the dynamic structural evolution of as-prepared CeO2/BiOCl precatalyst under realistic CO2 electroreduction conditions, by combining operando XRD, Raman and XAFS measurements. It has comprehensively been demonstrated that the real active catalyst for CO2 reduction is regenerative CeO2/Bi interface structure with increased Ce3+ species. High Faradaic efficiency and stability for formate formation are finally exhibited onto the derived CeO2/Bi interface structure. D2O isotope labeling results have verified that the hydrogen elements of formate product originate from water activation. We have revealed that the regenerative CeO2/Bi interface sites can properly promote water activation to supply hydrogen source for the formate formation, and lower the energy barrier of the CO2 protonation into the key intermediate *OCHO. This work provides insights into structural evolution and activity origin of catalysts under realistic working conditions, and highlights the importance of mechanism study and catalyst design based operando feedback information.

METHODS

Synthesis of CeO2/BiOCl and BiOCl

CeO2/BiOCl was synthesized through a propylene oxide (PO)-assisted hydrolytic process. Typically,
BiCl₃ (1.5 mmol) and CeCl₃·7H₂O (0.5 mmol) were firstly dissolved in deionized water (4.5 ml). Then PO (1.3 ml) was added in the above liquid to obtain the liquid emulsion. The solution was stirred for 6 hours and then aged for 6 hours. The obtained precipitate was collected by centrifuging and washed five times with deionized water and ethanol, then dried at 60°C for 8 hours in the air. Finally the obtained product was placed into a muffle furnace and heated to 400°C for 2 hours at a rate of 3°C/min. BiOCl counterpart was prepared with the similar method except that CeCl₃·7H₂O was not added.

**Electrochemical measurements**

Electrochemical measurements were performed in a three-electrode two-compartment cell separated by Nafion 117 membrane in an electrochemical workstation (CHI 660E). ¹H NMR spectroscopy was used to analyze liquid products. The ¹H NMR spectra were recorded on an Ascend 600-MHz Unity plus spectrometer (Bruker). The electrolyte (0.5 mL) was mixed with deuterated water (0.1 mL), using 1% tetramethylsilane (TMS) as internal standard. CO₂RR measurements in D₂O solution were carried out with similar processes to that in H₂O. The total amount of formate (HCOO⁻ and DCOO⁻) in electrolytes was quantified by High Performance Liquid Chromatography (HPLC). ¹H NMR was used to determine the amount of HCOO⁻ product. The concentration of formate was quantitatively determined from its NMR peak area relative to the internal standard by using the calibration curve for standard HCOOK solutions (Supplementary Fig. 22).

**SUPPLEMENTARY DATA**

Supplementary data are available at NSR online.

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**AUTHOR CONTRIBUTIONS**

C.Z.L. and H.L.J. planned the project and designed the experiments. R.C.P. carried out most of the sample preparation and material measurements. P.F.T. performed DFT calculations and analyzed the data. X.Z.S. and Y.W. conducted operando XAS test. X.L.Y. and Y.H.Z. contributed to the STEM analysis. L.S. helped to conduct XAS analysis. M.H.Z. helped to analyze operando Raman and FTIR data. R.C.P., P.F.T., H.L.J. and C.Z.L. co-wrote the paper. All authors discussed the results and commented on this manuscript.

**Conflict of interest statement.** None declared.

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