Active/Conductive Layer Stacked Superlattices for Highly Selective CO₂ Electroreduction

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Article

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Abstract

Metal oxides are the archetypal CO₂ reduction reaction (CO₂RR) electrocatalysts, yet the inevitable self-reduction will enhance competitive hydrogen evolution and lower the CO₂RR selectivity. Herein, we propose a tangible superlattice model of alternating metal oxide and sulfide sublayer in which electrons are rapidly exported through the conductive metal sulfide layer to protect the active oxide layer from self-reduction. Taking BiCuSeO superlattices as a proof-of-concept, a comprehensive characterization reveals that the active [Bi₂O₂]²⁺ sublayers retain oxidation states rather than their self-reduced Bi metal during CO₂RR because of the rapid electron transfer through the conductive [Cu₂Se₂]²⁻ sublayer. Theoretical calculations uncover the high activity over [Bi₂O₂]²⁺ sublayers due to the overlaps between the Bi p orbitals and O p orbitals in HCOO* intermediate, thus achieving over 90% formate selectivity in a wide potential range from -0.4 to -1.1 V. This work broadens the horizons of studying and improving the CO₂ electroreduction properties of metal oxide systems.

Introduction

Electrochemical CO₂ reduction (CO₂RR) to high value-added carbon-based products has received extensive interest and represents a boulevard from the renewable electricity sources to chemical and fuel production^{1, 2, 3, 4, 5}. Formate, which is widely used as most kinetically accessible feedstock in the field of pharmaceutical, textile, and energy, is an attractive liquid product of CO₂RR^{3, 6, 7, 8}. Metal oxides (such as SnO₂, Bi₂O₃, In₂O₃) as the most common and widely available catalysts have been extensively explored to achieve CO₂ electroreduction to formate with considerable activity^{6, 9, 10, 11, 12, 13, 14}. The development of advanced in situ characterization uncovers that metal oxides can undergo in situ self-reduction to zero-valence metal during the CO₂RR (Fig. 1a)^{15, 16}. Along the way, substantial efforts have been devoted to exploring the efficient catalysts derived from these metal oxides^{17, 18, 19, 20, 21, 22}. However, with this self-reduction, the competitive hydrogen evolution reaction (HER) performance of the derived metal catalysts will gradually dominate^{1, 16, 22, 23, 24, 25, 26}, resulting in their CO₂RR activity being difficult to maintain in a wide potential window. Actually, this spontaneous self-reduction of metal oxides is contradictory to the high selective CO₂RR performance. More importantly, due to the untenable oxidation state during the CO₂RR, unraveling the catalytic mechanism of metal oxides will be inaccessible. Therefore, developing electrocatalysts based on metallic oxidation state rather than their self-reduction is highly desirable for performance optimization and mechanism exploration, which remains to be an enormous challenge.

Recently, several representative reports have put forward metal oxides–support interaction system to stabilize oxidation state during the CO₂RR (Fig. 1a)^{17, 27, 28, 29, 30, 31}, especially metal oxides–carbon^{17, 21, 27, 30, 31, 32}, in which carbon layer acts as a conductive layer to quickly conduct electrons and prevent the active oxides from being reduced. Notwithstanding these efforts, the composite catalytic materials have their own inevitable weaknesses, mainly poor interface contact^{17, 27, 30, 31}. As a result, a large number of

oxides in non-interface areas may still be self-reduced^{10, 32}. Inspired by the strengths and weaknesses of this structural model, finely stacking ultrathin oxides layer upon layer on conductive substrates will maximize the potential of such models but call for extremely rigorous synthesis method.

Focus on this vision, natural superlattice, which consist of one-by-one vertically stacked plural subunits, will be motivated as perfect and tangible models. In a natural superlattice, one can obtain metal oxide layer and conductive layer at the same time by elaborately designing the prototype of each subunit (Fig. 1a), in which the conductive layer rapidly conducts electrons to protect the active center of the oxide layer to drive the activation of CO₂. Guided by this delicate avenue, a typical natural superlattice, BiCuSeO oxyselenides (Fig. 1b)^{33, 34, 35}, which consists of conductive [Cu₂Se₂]²⁻ and insulating [Bi₂O₂]²⁺ sublayers stacking alternately along *c*-axis, is thought to interplay the Cu-Se layer/ Bi-O layer for efficient CO₂ electroreduction. More characteristically, Bi-based oxides are the first self-reduction phenomenon discovered and still considered to be highly promising candidates for selective formate production^{21, 32, 36, 37, 38}. Therefore, natural BiCuSeO superlattice provides an excellent opportunity to obtain high efficiency CO₂ properties on metal oxidation state rather their self-reduction and explore their structure-activity relationships

Herein, we propose BiCuSeO nanosheets (Ns) as an example and utilize alternately stacked insulating [Bi₂O₂]²⁺ and conductive [Cu₂Se₂]²⁻ in its superlattices as active/conductive sublayer to stabilize metal oxidation state for high CO₂RR activity and selectivity. Specifically, X-ray photoelectron spectroscopy (XPS), synchrotron-based X-ray absorption near-edge structure (XANES) spectroscopy and extended X-ray absorption fine structure (EXAFS) studies consistently confirm that the Cu-Se sublayers in the BiCuSeO superlattices mainly conducts electrons so that the highly active Bi in the Bi-O layer still holds their oxidation state fine rather than self-reduced zero-valence Bi metal during the CO₂RR. Furthermore, density functional theory (DFT) simulation reveals that Bi-O coordination in [Bi₂O₂]²⁺ exhibits a strong coupling effect with its Bi *p* orbitals overlapping with O *p* orbitals in HCOO* and enables a highly selective CO₂RR to formate. Benefitting by the interplay of Cu-Se layer/ Bi-O layer, natural BiCuSeO superlattices exhibit a high catalytic selectivity featured by formate Faradaic efficiency FE of > 90% at a wide potential range from - 0.4 to -1.1 V. Importantly, the catalytic model, active/conductive layer alternately stacked natural superlattices, could provide valuable insights for the development of highly efficient CO₂RR catalysts and beyond.

Results

Structural characterizations of BiCuSeO Ns. Herein, ultrathin BiCuSeO nanosheets are synthesized by using polyvinylpyrrolidone (PVP) as the control agent *via* a mild hydrothermal route. X-ray diffraction pattern (XRD) and Raman spectrum, shown in Supplementary Fig. S1, all solidly index to the successful synthesis of the crystalline BiCuSeO phase with high purity. The atomic force microscopy (AFM) and transmission electron microscopy (TEM) characterizations in Fig. 1c, d and Supplementary Fig. S2 reveal sheet-like morphology with an average thickness of ~ 9.2 nm of obtained BiCuSeO. The high-resolution

TEM (HRTEM) image shows two sets of mutually perpendicular lattice fringes with a spacing of ~ 0.28 nm (Fig. 1e), corresponding to the (110) and (1 $\bar{1}$ 0) planes of tetragonal BiCuSeO respectively. A single set of diffraction spots with a fourfold symmetry in the selected area electron diffraction (SAED) pattern (Fig. 1f) illustrates the high orientation along *c* axis of the as-obtained BiCuSeO Ns, which is consistent with HRTEM analysis. Additionally, the energy dispersive spectroscopy (EDS) mapping analysis points out the uniform distribution of Bi, Cu, Se and O elements (Fig. 1g). Consequently, all above structural characterization results evidently verify the successful synthesis of ultrathin BiCuSeO single-crystal nanosheets.

Electrochemical performances of BiCuSeO in 0.5 M KHCO₃. The electrochemical performance of the as-fabricated BiCuSeO is evaluated using a three-electrode flow cell in CO₂-saturated KHCO₃ aqueous solution (Supplementary Fig. S3). To investigate the effect of Bi and Cu elements in BiCuSeO for CO₂RR, the electrocatalytic activities of Bi₂O₃ and Cu₂Se Ns (Supplementary Fig. S4 and S5) are also tested for comparisons. First, the linear sweep voltammetry (LSV) curves are conducted in a potential range of 0 $\sim$ -1.1 V (the reversible hydrogen electrode, RHE, all the potentials mentioned in the following are RHE). As shown in Fig. 2a, BiCuSeO reveals significantly improved current density and more positive onset potential than Cu₂Se and Bi₂O₃, demonstrating its best electrocatalytic performance for CO₂RR. To identify the products and their Faraday efficiency (FE) at different potentials, we conduct the electrolysis at a variety of constant potentials from -0.4 to -1.1 V and collected samples for the further test. From the chronoamperometry curves (Fig. 2b), the current density is consistent with LSV curves and remains steady, suggesting a good electrochemical stability of BiCuSeO catalysts. Accordingly, the gaseous and liquid products are quantitatively analyzed by online gas chromatograph (GC) and ¹H nuclear magnetic resonance (¹H NMR) spectroscopy, respectively. The GC and NMR results display that formate is the predominant product, accompanied with minor amounts of H₂ and CO gas. Apparently, the BiCuSeO shows a high selectivity towards formate production, and its FE (FE_{formate}) is over 90% in a wide potential window ranging from -0.4 to -1.1 V and a maximum value can reach to $\sim 93.4\%$ at -0.9 V, while the FE for CO and H₂ gas are $\sim 2.4\%$ and $\sim 2.4\%$, respectively (Fig. 2c). Noticeably, the overpotential for formate generation is as low as 190 mV, which is smaller than that of most other Bi-based catalysts^{11, 30, 31, 36, 37, 38, 39, 40, 41, 42, 43, 44, 45, 46, 47}. Moreover, the FE_{formate} of for BiCuSeO are much higher than that of Cu₂Se (the maximum FE_{formate} is $\sim 60\%$) and Bi₂O₃ (the maximum FE_{formate} is $\sim 85\%$) at the tested potentials, indicating that BiCuSeO Ns is more inclined to yield the formate product (Fig. 2d). Furthermore, the calculated formate partial current densities (*j*_{formate}) of BiCuSeO are significantly larger than that of Cu₂Se and Bi₂O₃ at same potentials, and the maximum value can reach ~ 47.5 mA cm⁻² at -1.1 V without IR compensation (Fig. 2e). This result underlies that the CO₂RR on BiCuSeO Ns electrocatalysts is significantly more efficient and selective. Gratifyingly, compared with other state-of-the-art Bi-based catalysts^{11, 30, 31, 36, 37, 38, 39, 40, 41, 42, 43, 44, 45, 46, 47}, BiCuSeO can hold the outstanding formate selectivity over a wide potential window (> 90% from -0.4 to -1.1 V, Fig. 2f). In general, the CO₂ reduction rate will increase obviously in the alkaline electrolyte. Therefore, the electrocatalytic performance of CO₂ are also

tested in 1 M KOH and exhibit similar outstanding formate selectivity over a wide potential window and impressive current density $\sim 267 \text{ mA cm}^{-2}$ at -1.1 V (Supplementary Fig. S6). In addition, Tafel slope is determined by using the logarithm of formate partial current density against with the applied potentials to evaluate the reaction kinetic of CO_2 RR^{3, 48}. The calculated Tafel slope of BiCuSeO is about 568.6 mV dec^{-1} , which is much smaller than that of Cu_2Se (1052.4 mV dec^{-1}) and Bi_2O_3 (674.4 mV dec^{-1}), suggesting its favorable kinetics of BiCuSeO for formate generation (Fig. 2g). Furthermore, electrochemical reduction reaction for CO_2 at a fixed potential of -0.9 V is carried out over an extended period to evaluate the stability of the BiCuSeO. As shown in Fig. 2h, the total current density stabilizes at about 32 mA cm^{-2} together with an average $\text{FE}_{\text{formate}}$ of $\sim 93\%$ over 10 h. Remarkably, by the SEM images, the morphology of BiCuSeO catalysts is substantially preserved (Supplementary Fig. S7). To sum up, all the above results indicate that the BiCuSeO exhibits splendid formate selectivity in a wide potential window for CO_2 RR.

Intermediates detection. To monitor the reaction process and the intermediate species of CO_2 RR^{15, 49}, we carry out in situ electrochemical Raman spectroscopy tests (Fig. 3a). Two obvious Raman peaks at 1160 and 1540 cm^{-1} are detected at -0.5 V or lower potentials in Fig. 3b, c. Specifically, the peaks at 1160 cm^{-1} can be ascribed to the C = O stretching vibration of surface adsorbed carbonate ($\nu_s \text{CO}_2^{\cdot -}$) during the CO_2 RR electrolysis process (Fig. 3b, c, Supplementary Fig. S8)^{50, 51, 52}. Meanwhile, the peaks located at 1540 cm^{-1} are vibrational fingerprints of asymmetric C–O stretching vibration modes of proton-trapped carboxylate $^*\text{CO}_2^{\cdot -}$ radicals ($\nu_{\text{as}} \text{CO}_2^{\cdot -}$)^{50, 51, 52}. Therefore, both peaks are attributed to the key intermediates HCOO^* for formate product during electroreduction CO_2 ^{51, 52, 53}, which also confirm that CO_2 could be directly activated and reduced into formate with lower potential on BiCuSeO catalysts. Notably, their peak intensity gradually increases as the applied potentials and reached a high point at -0.7 V. This variation trend of characteristic peak intensity with potentials may depend on the trade-off between adsorption and transformation of intermediate products. Moreover, the time-count in situ Raman spectra at -0.6 and -0.7 V show that the peaks intensity of the crucial intermediates for formate gradually strengthen with expanding time (Fig. 3d, e), resulting from a favorable adsorbing and proton-trapping capacity of formate intermediates. This indicates a step-by-step reaction process for formate generation from CO_2 . No obvious band associating with C–O stretching or C = O stretching of $^*\text{COOH}$ intermediate for CO product indicating that the formation of CO on BiCuSeO is almost suppressed^{50, 51, 52, 54}, which is consistent with the above experimental FE results. To validate the binding affinity of $\text{CO}_2^{\cdot -}$, the adsorption of OH^- as a surrogate for $\text{CO}_2^{\cdot -}$ is detected by oxidative LSV scans in a N_2 -bubbled 0.1 M NaOH electrolyte. Figure 3f reveals that the potential for surface OH^- adsorption on the BiCuSeO is lower than that for Bi_2O_3 and Cu_2Se Ns. This result combined with the Raman analyses adequately illustrates that the BiCuSeO possesses a stronger adsorption affinity of OH^- , and hence they could efficiently stabilize the $\text{CO}_2^{\cdot -}$ intermediate, finally facilitating formate production.

Structural transformation, XAFS, XPS and TEM characterizations of BiCuSeO after CO₂ RR. Actually, metal oxides based electrocatalysts would inevitably undergo spontaneous reduction under the function of negative potential during CO₂RR process¹⁶. XRD pattern and Raman spectrum in Supplementary Fig. S9a-c show that the crystalline BiCuSeO phase can still be mainly retained with partial Se escaping during CO₂RR process. To further determine whether the structure of the Bi-O layer can be maintained as expected, the synchrotron radiation X-ray absorption fine structure (XAFS) spectroscopy were performed. Specifically, Bi L3-edge XAFS measurements are explored and presented in Fig. 4a. Both the absorption edge and white line peak of the XANES for BiCuSeO nearly overlaps with that of Bi₂O₃ reference, suggesting the Bi³⁺ species of Bi atoms in BiCuSeO. After CO₂RR, the absorption edge of BiCuSeO_R (the BiCuSeO after CO₂RR is denoted as BiCuSeO_R) only slightly shifts towards a lower energy, indicating that the oxidation state of Bi mainly retains. Furthermore, the Fourier transform (FT) of the EXAFS curve is resolved to evaluate the Bi local environment at atomic-level (Fig. 4b). The intense peak of BiCuSeO_R is located 1.63 Å (without chemical shift), which is still consistent with the pristine BiCuSeO and can be attributed to the first Bi-O coordination shell. The relatively controlled peak weakening further explains that most of the Bi-O bonds of BiCuSeO are maintained after CO₂RR. Meanwhile, wavelet transform (WT) is used to precisely analyze the Bi L3-edge extended X-ray absorption fine structure (EXAFS) oscillations. The WT contour plots of BiCuSeO_R display only one intensity maximum at 1.6 Å, which is apparently corresponding to the Bi-O coordination with BiCuSeO rather than the Bi-Bi in Bi powders. Notably, combined with its crystal structure, the length of Bi-O bond in the BiCuSeO superlattice is significantly larger than that in the common Bi₂O₃, showing a new type of Bi-O coordination structure for CO₂RR. Furthermore, to clearly illustrate the coordination states, the intense peak is finely fitted and the fitting result suggests that it consists of two peaks superimposed, named as Bi-O₁ (2.13 Å) and Bi-O₂ (2.27 Å) (Supplementary Fig. S10-12, Table S1). The Bi-O₂ is attributed to the lattice bond in BiCuSeO, and the coordination number (CN) is calculated to be 2.5 (Supplementary Table S1), which is close to the value for BiCuSeO (CN = 4), further illustrating that only a small amount of reduced Bi³⁺ after CO₂RR different from contrastive Bi₂O₃ Ns. The fitted coordination number of metal Bi-Bi bond (3.09 Å) for BiCuSeO_R is only 0.3 (Supplementary Table S1), which also supports the above conclusion. Combined with in situ Raman results (Fig. 3), the appearance of the Bi-O₁ can be reasonably attributed to chemisorbed *OH and HCOO* species, suggesting the effective adsorption of intermediates in CO₂RR. Taken together, all these results clearly illustrate that Bi sites are still retained in the oxidation state under the negative potential during CO₂RR as assumed, which certainly is conducive to drive the conversion of CO₂ to formate (Fig. 4a, b, e, Supplementary Fig. S10-12, Table S1). By contrast, combined with XAFS, XRD and XPS, Bi₂O₃ does essentially transform the metal Bi as reported (Fig. 4a, b, e, Supplementary Fig. S16).

In addition to the Bi-O bond, it is noteworthy that the Bi-Se bond weakens dramatically, with the coordination number reduced from 8 to 0.8 (Fig. 4b, Supplementary Table S1), which results from the precipitation of Se. In general, metal selenides are very sensitive and may undergo structural evolution to form metal oxide catalysts during the electrochemical process. Meanwhile, Cu-Se sublayer as conductive

layer undertake electron transport, leading to the self-reduction. Therefore, the local structure of Cu-Se sublayers are also investigated by Cu K-edge XAFS spectra (Fig. 4c). First, the absorption edge for Cu K-edge XANES spectrum of BiCuSeO_R locates between Cu foil and BiCuSeO, implying that Cu⁺ species are partially reduced and the valence state of its Cu atoms is between 0 and + 1. Furthermore, EXAFS curves of Cu K-edge reveal that the main peak at 2.06 Å disappeared and two new characteristic peaks appeared at 1.93 Å and 2.58 Å for BiCuSeO_R (Fig. 4d, Supplementary Fig. S10, S11, S13, Table S1), respectively. Based on the comparison, the emergent peaks can be attributed to Cu-O bonds and metallic Cu-Cu bond. Meanwhile, the calculated coordination number for Cu-Se bonds, Cu-O bonds and metallic Cu-Cu bond are 0.7, 0.8 and 4, respectively (Supplementary Fig. S10, S11, S13, Table S1). Based on the above structural characteristics, it is reasonable to assume that in the process of CO₂ reduction, a large number of Se atoms overflow from the conductive Cu-Se lattice. To keep the structure stable, some of the space left are filled with ambient oxygen, while some of the copper atoms bonded directly (Fig. 5a). Similarly, the in situ XANES, EXAFS and XPS (Fig. 4f, Fig. 5a, Fig. 5e and Supplementary Fig. S14, S15, Table S1) conformably point to their structural features and further reinforce our inference. As a control, we also explore the structural evolution process of Cu₂Se during CO₂ reduction. Similar to other conventional selenides and Cu-Se layer of BiCuSeO, Se atoms are essentially escaped from the Cu₂Se lattice and thus completely transform into Cu and Cu₂O (Supplementary Fig. S17, S18).

To further confirm the structural features, X-ray photoelectron spectroscopy (XPS) are also carried out. From Fig. 5b, the intensity of two typical Se 3d characteristic peaks exhibit a sharp decrease for BiCuSeO_R compared to that for BiCuSeO^{34, 55}, suggesting that a large percentage of Se escape from the Cu-Se sublayers during the electrocatalytic reaction. Meanwhile, the indistinct Se distribution through the BiCuSeO_R nanosheet in EDS mapping explain the loss of Se (Fig. 5g), which are identical with XAFS and XPS results (Fig. 4, Fig. 5a, Supplementary Fig. S10-S15). Furthermore, the high-resolution O 1s XPS spectrum of pristine BiCuSeO (Fig. 5c) can be split into three deconvolution peaks at circa 529.37, 530.87, and 533.03 eV, which belong to Bi-O, Bi-OH, and surface-adsorbed oxygen species, respectively^{30, 31}. After CO₂RR, besides the peaks at circa 530 eV corresponding to Bi-O and 531.92 eV corresponding to Bi-OH, an intense peak with higher binding energy at 535.29 eV, arising from surface adsorbed carbonate species^{56, 57}, appear in the O 1s spectrum of BiCuSeO_R. These observations are in line with the corresponding Raman results (Fig. 3) and further suggests that the CO₂ molecules are stably adsorbed onto the surface of the BiCuSeO catalyst during the electrocatalytic CO₂RR. As expected, the XPS Bi 4f core-level spectra of BiCuSeO_R and BiCuSeO remain consistent (Fig. 5d), which confirms the existence of metallic Bi^{11, 47}. Interestingly, in addition to changes in the local structure and chemical states, the structural framework of the BiCuSeO superlattice tends to be stable during CO₂RR, which may be due to the mutual support of the sublayers (Fig. 5). In summary, XANES, EXAFS, XPS and HRTEM studies consistently confirm that the highly active Bi oxidation state can be stabilized by finely designing superlattices stacked with Bi-O layer and conductive Cu-Se layer (Fig. 4, Fig. 5, Supplementary S14, S15), which can undoubtedly contribute to high selective CO₂ electroreduction performance at a wide potential window and explore its structure-activity relationship.

DFT calculations. To explore the intrinsic origin of high formate selectivity and activity over the $[\text{Bi}_2\text{O}_2]^{2+}$ sublayers in BiCuSeO superlattice, DFT calculations are performed to investigate the electronic structure of catalyst as well as the strength of the interaction between catalytic interface and CO_2 molecular species (Supplementary Fig. S19a). Firstly, to verify whether the $[\text{Cu}_2\text{Se}_2]^{2-}$ sublayer of BiCuSeO_R alters and functions as conductive channel after the structural transformation, their electron charge density and density of states (DOS) are studied. Clearly, the typical positive charges feature localizes along $[\text{Cu}_2\text{Se}_2]^{2-}$ sublayers after structural transformation (Fig. 6a), suggesting $[\text{Cu}_2\text{Se}_2]^{2-}$ sublayers still maintains a good conductivity and can be employed as the conductive channel. Moreover, the total DOS (sum) of BiCuSeO_R in the neighborhood below the Fermi level is mainly contributed by bonding hybridized Cu d and Se p states from $[\text{Cu}_2\text{Se}_2]^{2-}$ sublayers (Fig. 6d), which is the origin endowing the conductive character. The sharp peak characteristic in the PDOS of Cu d orbital further illustrate a strong d electron localization, resulting in the localized charge distribution in $[\text{Cu}_2\text{Se}_2]^{2-}$ sublayers. More notably, different from pristine BiCuSeO reported previously³³, the DOS of BiCuSeO_R below Fermi level cross over Fermi surface, implying the typical semi-metallic/metallic nature and thus an enhanced conductivity for BiCuSeO_R after structural evolution. The above results and analyses consistently indicate that $[\text{Cu}_2\text{Se}_2]^{2-}$ sublayers in superlattice still maintain fine and even enhanced conductivity. Meanwhile, PDOS of Bi p and Bi s orbitals overlap with that of O p orbitals to a great extent, indicating a strong interaction between Bi atoms and O atoms, and the oxide state of Bi in $[\text{Bi}_2\text{O}_2]^{2+}$ sublayer is negligibly influenced by structural transformation and can be well retained (Fig. 6e). All of the above results show that $[\text{Cu}_2\text{Se}_2]^{2-}$ sublayer still functions as a conductive channel while $[\text{Bi}_2\text{O}_2]^{2+}$ sublayer maintain strong Bi-O coordination structure feature in BiCuSeO superlattices after structural transformation. To dive deep into the interaction process between catalytic interface and CO_2 molecules, we further calculate the charge density difference and DOS of HCOO*intermediate adsorbed BiCuSeO_R. The charge density difference (Fig. 6b, c, Supplementary Fig. S20) reveals that the charge transfers directly from Bi atoms in $[\text{Bi}_2\text{O}_2]^{2+}$ sublayers to O atoms in HCOO* intermediate, which is beneficial to activate CO_2 molecules as well as generate and stabilize formate intermediates HCOO* on BiCuSeO_R surface. Even more, HCOO* absorbed BiCuSeO_R displays a higher DOS value near the Fermi level than BiCuSeO_R, further suggesting that the good charge transfer from BiCuSeO_R towards formate intermediates HCOO* (Supplementary Fig. S21). Actually, large overlaps of Bi p states and O p states below the fermi level in the PDOS of HCOO* absorbed BiCuSeO_R (Fig. 6f, Supplementary Fig. S22) further point out that Bi atoms in $[\text{Bi}_2\text{O}_2]^{2+}$ layer of BiCuSeO_R have a strong interaction effect with the O atoms in HCOO* intermediates, which contributes to the absorption and stabilization of HCOO* intermediate on BiCuSeO_R surface. Taken together, new typical Bi-O oxide structure the $[\text{Bi}_2\text{O}_2]^{2+}$ sublayer endows strong activation capacity of CO_2 molecules and stabilization ability of intermediates HCOO*, resulting in a high activity for CO_2RR .

To better elucidate the high selectivity of CO_2RR , reaction Gibbs free energies (ΔG) for CO_2 electroreduction to formate on catalytic model (Supplementary Fig. S19) are calculated and presented in

Fig. 6g. For comparison, Gibbs free energies for CO₂ electroreduction to CO and competitive HER are also performed (Fig. 6h, i, Supplementary Fig. S19). The Gibbs free energies for HCOO* formation processes on four possible sites are all exergonic (ΔG_{HCOO^*} on sites 1–4 are – 0.4551, –0.4957, –0.4827, and – 0.4575 eV respectively), indicating their CO₂ activation and protonation processes are spontaneous. Whether CO₂ electroreduction to form *COOH or HER to form *H are endergonic ($\Delta G_{*_{\text{COOH}}} = 0.8994$, 0.8900, 0.8498, 0.8471 eV; $\Delta G_{*_{\text{H}}} = 0.7165$, 0.8614, 0.70244, 0.7035 eV), suggesting a much lower energy barrier for the formation of CHOO*, the crucial intermediate for generating formate. Interestingly, it can be observed that the energy barrier for CHOO* intermediate transformation to formate and subsequent desorption process is still smaller than that for CO and that for H₂. These results indicate that BiCuSeO_R thermodynamically enables the activation of CO₂ molecules to form HCOO* intermediate and thus further produce formate. Consistent of the predesigned scenario, the DFT calculation results solidly support that in natural BiCuSeO superlattices the [Cu₂Se₂]^{2–} sublayers conducts electrons, while the [Bi₂O₂]²⁺ sublayer act as the active center for the activation of CO₂ molecules and subsequent formation/stabilization of HCOO* intermediates, enabling highly selective CO₂ electroreduction to formate.

Discussion

In summary, we propose a tangible active/conductive layer alternately stacked natural superlattices for stabilizing metal oxidation state for high activity and selectivity CO₂RR performance. Taking the example of BiCuSeO, which consists of alternately stacked conductive [Cu₂Se₂]^{2–} and insulating [Bi₂O₂]²⁺ sublayers, a comprehensive characterization disclosed that Bi-O layers were retained to drive the activation of CO₂ molecules during CO₂RR on account of the electrons rapidly conducted through conductive [Cu₂Se₂]^{2–} sublayers. Furthermore, DFT calculations indicate that new Bi-O coordination in [Bi₂O₂]²⁺ exhibits a strong activating and stabilizing effect towards HCOO* intermediate with its Bi p orbitals overlapping with O p orbitals in HCOO* and enables a highly selective CO₂ electroreduction to formate. As a direct outcome, BiCuSeO natural superlattices is found to produce formate with an optimum FE of > 90% at a wide potential range from – 0.4 to –1.1 V in neutral electrolyte. Our work not only serves as a tangible model with active/conductive layer alternately stacked natural superlattices to suppress the reduction of the metal oxidation electrocatalysts for improving the CO₂RR selectivity but also introduces new coordination structures in designing new CO₂RR materials.

Methods

Synthesis of BiCuSeO Ns. Bi(NO₃)₃·5H₂O (~ 95 mg) is firstly added in a mixed solvent containing 5 mL ultra-pure water and 5 mL ethanol upon ~ 10 min magnetic stirring. When a milky white suspension is generated, selenourea (26 mg) is added with continued stirring. Then PVP (K30, 100 mg), Cu(NO₃)₂·3H₂O (~ 50 mg), KOH (120 mg), and NaOH (320 mg) are subsequently added with continuous stirring to obtain a black suspension. Afterwards, the contents are transferred into a 50 ml Teflon lined stainless steel

autoclave and heated at 180°C for 24 h. After cooling to room temperature naturally, the black precipitate is washed with H₂O and ethanol and then naturally dried under ambient conditions.

Synthesis of Cu₂Se Ns. Cu₂Se NS is prepared according to the reference⁵⁸. 157 mg Se powder, 5 g NaOH, and 704 mg ascorbic acid are firstly dissolved in 20 mL of H₂O at 50°C, and then added a pre-made aqueous solution containing 199 mg Cu(CH₃COO)₂·H₂O, 100 mg beta cyclodextrin and 30 mL H₂O. The mixed solution is placed in a Teflon-lined stainless steel autoclave and hydrothermally treated at 180°C for 6 h.

Synthesis of Bi₂O₃ Ns. Bi₂O₃ Ns is prepared according to the reference^{21, 59}. 0.5 mmol Bi(NO₃)₃·5H₂O dissolved into 8.5 mL ethylene glycol and 4.3 mL ethanol, and placed in a Teflon-lined stainless steel autoclave and hydrothermally treated at 160°C for 5 h.

Characterizations. The samples are tested by X-ray diffractometer (XRD, Cu K α , λ = 1.5405 Å, D2 PHASER, Bruker), atomic force microscope (Dimension Icon, Bruker), X-ray photoelectron spectroscopy (XPS, AXIS-ULTRA DLD-600W), atomic force microscope (AFM, Dimension Icon, Bruker), confocal Raman system (Alpha 300RS+, WITec), scanning electron microscope (SEM, FEI quanta 650) and high-resolution transmission electron microscopy (HRTEM, FEI Tecnai G2 F30) equipped with an X-ray energy dispersive spectrometer (EDS). X-ray absorption fine structure spectra (XAFS) are acquired at BL14W1 beamline at Shanghai Synchrotron Radiation Facility (SSRF).

Electrochemical Measurements. CO₂RR performances of the various samples are tested by using a three-electrode flow cell system in CO₂-saturated 0.5 M KHCO₃ aqueous solution. All electrochemical measurements are conducted on a CHI 760E electrochemical workstation (CH instrument, Shanghai, China). Catalyst deposited on gas diffusion layer with 1 cm² working area is used as the working electrode (WE). The Ag/AgCl electrode and platinum plate are employed as the reference electrode (RE) and counter electrode (CE), respectively. During the electrochemical measuring, CO₂ is pumped into the cathode chamber with a constant flow rate (20 mL min⁻¹). The gas products are detected by using an in situ connected gas chromatograph instrument (PANNA, A91lus). The liquid products are analyzed by nuclear magnetic resonance (NMR) spectrometer (Bruker Ascend TM 600 MHz). The Faradaic efficiency (FE) during CO₂RR is calculate by the equation, $FE = Q_i/Q_t = (N_i \times n \times F)/Q_t$, where Q_i is the charge amount for product reducing, Q_t is the total charge consumed, N_i is the product molar amount, n is the electrons transferring number (which is 2 for formate, H₂ and CO), and F is the Faradaic constant (96485 C mol⁻¹).

In Situ Raman Measurements. In situ Raman measurements are conducted by employing a top-plate cell euphotic device shown in Fig. 3a, which is connected with a electrochemical workstation. Three-electrode (WE, RE and CE) and electrolyte are same as that used in the anterior electrochemical measurements. Prior to Raman measurements, CO₂ is bubbled into electrolyte. The in-situ Raman spectra are acquired from a confocal Raman spectroscopy (Alpha300, WITec) by using 532 nm laser source.

In Situ XAFS Measurements. In situ XAFS measurements are conducted on a home-made homemade equipment (Fig. S14). XANES is acquired at the BL14W1 beamline of the Shanghai Synchrotron Radiation Facility (SSRF), China. The absorption edge position (E_0) is calibrated by employing Cu foil, and all the XANES data are collected by fluorescence mode. Every XANES spectrum is tested two or three times.

DFT Calculations. All the calculations were carried out based on density functional theory (DFT) as implemented in the Vienna Ab initio Software Package code within the Perdew-Burke-Ernzerhof (PBE) generalized gradient approximation and the projected augmented wave (PAW) method⁶⁰. The cutoff energy of the plane-wave basis is 500 eV. The BiCuSeO_R structural models was relaxed by $4 \times 4 \times 1$ Monkhorst – Pack grid with the solvation correction^{61, 62}. The convergence criterion for the electronic self-consistent iteration and force was set to 10^{-5} eV and 0.01 eV/Å, respectively. A vacuum slab of greater than 10.0 Å was selected to avoid periodic interactions. The Gibbs free energy change (ΔG) was calculated at 298.15 K according to the computed hydrogen electrode mode^{63, 64, 65}.

Declarations

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Contributions

Y. L. and T. Z. conceived and directed the project. Y. L. and J. D. designed the experiments. J. D. carried out the experiments. J. D. and Y. Z. performed and analyzed the DFT calculations. J. D., R. Y., and B. W. performed the XAFS and the in situ Raman spectroscopy. Y. L. and J. D co-wrote the paper. H. L. and T. Z. revised the paper. All authors discussed the results and assisted during manuscript preparation. J. D. and Y. Z. contributed equally to this research.

Competing interests

The authors declare no competing interests.

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Figures

Figure 1

Design scheme and structural characterizations of BiCuSeO superlattice nanosheets. a Schematic illustration of exploring single-phase materials with active/conductive layer alternately stacked superlattices. I Pure metal oxides. II Metal oxides– support interaction system. III Superlattice consisting

of one-by-one vertically stacked active-layer (metal oxides) and conductive layer subunit. b Structural model of BiCuSeO superlattice. c AFM image. d TEM image. e HRTEM image. f The corresponding SAED pattern. g EDS mapping images.

Figure 2

CO₂RR performance in 0.5 M KHCO₃. a LSV curves of BiCuSeO, Cu₂Se and Bi₂O₃ Ns without IR compensation. b Chronoamperometric curves at different potentials. c FE of formate, CO and H₂ for BiCuSeO Ns. d FE_{formate}, e J_{formate} and g Tafel slope comparisons of BiCuSeO, Cu₂Se and Bi₂O₃ Ns. f FE_{formate} comparison among the reported Bi-based catalysts and the BiCuSeO11, 30, 31, 36, 37, 38, 39, 40, 41, 42, 43, 44, 45, 46, 47. h 10 h Chronoamperometry results for BiCuSeO at -0.9 V.

Figure 3

Intermediates detection on BiCuSeO during CO₂RR. a Schematic illustration of in situ Raman measurement device during CO₂RR. b, c Potential-dependent and d, e time-dependent in situ Raman spectra of BiCuSeO catalysts in 0.5 M KHCO₃ solution under CO₂ bubbling. f Single oxidative LSV scans in N₂-saturated 0.1 M NaOH solution for BiCuSeO, Cu₂Se and Bi₂O₃ Ns.

Figure 4

XAFS characterizations of BiCuSeO after CO₂RR. **a** Bi L3-edge XANES and **b** corresponding FT-EXAFS spectra of BiCuSeO after CO₂RR. **c** Cu K-edge XANES spectra and **d** corresponding FT-EXAFS spectra of BiCuSeO after CO₂RR. Wavelet transform of the k₃-weighted EXAFS data of **e** Bi L3-edge and **f** Cu K-edge.

Figure 5

Structural evolution and composition analyses of BiCuSeO after CO₂RR. a Schematic illustration of the in situ structural evolution for BiCuSeO. b Se 2d, c O 1s, d Bi 4f and e Cu 2p XPS spectra for BiCuSeO catalysts before and after CO₂RR. f TEM and (g) the corresponding EDS mapping images of BiCuSeOR.

Figure 6

DFT calculations. a Charge density of BiCuSeO after CO₂RR. b Charge density difference of key reaction intermediates HCOO* on BiCuSeO during CO₂RR. The isosurfaces level is 0.002213 au. The yellow and blue shadows correspond to the charge accumulation and depletion, respectively. c Corresponding slice image of Fig. 6b along (010) face. d Total density of states (Sum), Cu d, Bi p and Se p orbitals PDOS, and O p orbitals PDOS obtained respectively from BiO and CuSe layers for BiCuSeO during CO₂RR. e O p, Bi p, Bi s and Cu p orbitals PDOS of BiCuSeO during CO₂RR. f PDOS of p orbitals for Bi and O atoms on BiO layer, PDOS of p orbitals for O and C atoms from HCOO*, and PDOS of s orbital from the adsorbed HCOO*. Gibbs free energy diagram of g CO₂ electroreduction to formate, h CO₂ electroreduction to CO, and i HER.

Supplementary Files

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