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We report significantly enhanced electrochemical CO\textsubscript{2} reduction (ECR) to C\textsubscript{2}H\textsubscript{4} by tuning the interface of a metal oxide composite (CuO\textsubscript{x}/HfO\textsubscript{2}), enabling a C\textsubscript{2}H\textsubscript{4} faradaic efficiency as high as 62.6 ± 1.3\% at 300 mA cm\textsuperscript{-2}, in contrast to only 11.6 ± 1.6\% over pure CuO. Collective knowledge from multiple control experiments, density functional theory calculations, and operando Raman study reveals that HfO\textsubscript{2} greatly strengthens CO\textsubscript{2} adsorption and also stabilizes the Cu\textsuperscript{+} species during the ECR, thus benefiting binding of *CO for further C–C coupling to yield C\textsubscript{2}H\textsubscript{4}. This work offers a simple and effective avenue to enhancing the ECR to yield C\textsubscript{2}H\textsubscript{4}.

Burning of fossil fuels leads to a dramatic increase in CO\textsubscript{2} emission, causing severe climate change.\textsuperscript{1} Electrochemical CO\textsubscript{2} reduction (ECR) into fuels and valuable feedstocks powered by renewable electricity, provides a promising route to alleviate global warming and simultaneously close the carbon loop.\textsuperscript{2} A plethora of electrocatalysts including metals,\textsuperscript{3,4} metal oxides,\textsuperscript{5,6} transition metal dichalcogenides,\textsuperscript{7,8} metal-organic frameworks,\textsuperscript{9,10} and single-atom catalysts\textsuperscript{11,12} have been developed for the ECR. Among these materials, Cu-based catalysts are promising for selectivity towards C\textsubscript{2}, (containing two or more carbon atoms) products due to favourable d-band levels and moderate CO binding energies.\textsuperscript{13,14} ECR to ethylene (C\textsubscript{2}H\textsubscript{4}) is appealing because this compound is highly demanded as a feedstock in industry and is also widely utilized as plant growth regulator for ripening fruits. However, it is still a formidable C–C coupling energy barrier.

It’s generally surmised that C\textsubscript{2}H\textsubscript{4} is obtained through dimerization of a common *CO (* denotes adsorption site) intermediate via the following possible steps 1) *CO → *C\textsubscript{2}O → *COCOH → *CH\textsubscript{2}CHO → C\textsubscript{2}H\textsubscript{4}; 2) *CO → *CHO → *COCHO → *COCHOH → C\textsubscript{2}H\textsubscript{4}; 3) *CO → *CHO → *OHCCOH → *CH\textsubscript{2}CHOH → *CH\textsubscript{2}CH\textsubscript{2} → C\textsubscript{2}H\textsubscript{4}.\textsuperscript{15} Under such circumstance, optimizing the binding strength of the *CO intermediate and lowering the *CO coupling barriers as well as concurrently suppressing the excessive H adsorption (to alleviate the parasitic HER and formation of CH\textsubscript{4}) are critical to promote CO\textsubscript{2} reduction selectively to C\textsubscript{2}H\textsubscript{4}. Herein, we demonstrate for the first time facile synthesis of a CuO\textsubscript{x}/HfO\textsubscript{2} heterostructure with large and intimate contact interface. HfO\textsubscript{2} is selected to construct the interface by taking advantage of its low cost, outstanding thermal and chemical stability, strong mechanical properties, high surface basicity, and exceptional CO\textsubscript{2} adsorption capability. Of particular interest is that introduction of the reducible HfO\textsubscript{2} can evidently stabilize Cu\textsuperscript{+} against its further reduction during electrolysis, thereby remarkably enhancing the ECR yield to C\textsubscript{2}H\textsubscript{4}. The ECR activity is tunable by adjusting the Cu-to-Hf molar ratio with an optimal value of 3:2, giving rise to a C\textsubscript{2}H\textsubscript{4} formation rate of 62.6 ± 1.3\% at 300 mA cm\textsuperscript{-2} in a flow reactor, exceeding bare CuO and many previously reported Cu-based catalysts.

The CuO\textsubscript{x}/HfO\textsubscript{2} composite catalysts were prepared through a simple hydrothermal method based on the coprecipitation of Cu(AC\textsubscript{2})\textsubscript{2}H\textsubscript{2}O and HfCl\textsubscript{4} in alkaline medium. Shown in Fig. 1a and Fig. S1 are the X-ray diffraction (XRD) patterns of CuO\textsubscript{x}/HfO\textsubscript{2} with various HfO\textsubscript{2} loadings, along with pure CuO and HfO\textsubscript{2} synthesized in a similar fashion. For CuO\textsubscript{x}/HfO\textsubscript{2}, the diffraction peaks at ~24.2, 28.4, 31.7, 41, 45.8, 50.4, and 55.6° can be well attributed to the (111), (111), (211), (202), (220), and (221) reflections of monoclinic HfO\textsubscript{2} (JCPDS no.: 078–0049), respectively. Broad and intense diffraction peaks located at ~35.5, 38.7, 48.7, 61.5, and 68° are assigned to the (111), (111), (202), (113), and (220) planes of monoclinic CuO (JCPDS no.: 080–1916). Interestingly, a diffraction peak at ~36.4° was also identified belonging to the (111) plane of cuprous oxide (CuO) (JCPDS no.: 078–2076), indicating the formation of Cu\textsuperscript{+} in the CuO\textsubscript{x}/HfO\textsubscript{2} samples.

The wide-scan X-ray photoelectron spectroscopy (XPS) spectrum of the CuO\textsubscript{x}/HfO\textsubscript{2} shows the predominant presence of Cu\textsuperscript{+}, O, and Hf elements without other impurities in the sample (Fig. S2a). Fig. 1b presents the Cu 2p XPS spectra of pure CuO and CuO\textsubscript{x}/HfO\textsubscript{2}, which displays a spin-orbit split doublet with Cu 2p\textsubscript{3/2} at ~954.1 eV and 2p\textsubscript{1/2} at 934.2 eV arising from Cu\textsuperscript{2+} species.\textsuperscript{16} There also exist three apparent Cu\textsuperscript{2+} satellites with binding energies (BEs) at ~961.1, 942.3, and 939.9 eV. For CuO\textsubscript{x}/HfO\textsubscript{2}, a doublet with Cu 2p\textsubscript{3/2} at ~952.1 eV and 2p\textsubscript{1/2} at 932.2 eV can be deconvoluted, signifying the existence Cu\textsuperscript{2+} moieties.\textsuperscript{6} The Cu LMM Auger excitation spectra (Fig. S2b) verified the presence of Cu\textsuperscript{2+} with a characteristic Auger peak at ~570.1 eV in CuO\textsubscript{x}/HfO\textsubscript{2},\textsuperscript{17} while no Cu\textsuperscript{2+} signal at about 568 eV was discernible. The Cu\textsuperscript{+} content in the catalyst could be readily modulated by altering the Cu-to-Hf molar ratio (Fig. S3

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Electronic Supplementary Information (ESI) available: [Experimental and relevant Please do not adjust margins
and Table S1), approaching 43.6% at the Cu-to-Hf molar ratio of 3:2. The BEs of the HF 4f peaks in the CuO/HfO2 shift markedly to higher values relative to pure HfO2 (Fig. S4a), indicative of electron transfer from Hf to Cu resulting in the formation of Cu2+ in the hybrid. The O 1s spectra can be deconvoluted into three subspectra (Fig. S4b) at about 532.4, 530.8, and 529.5 eV, corresponding to surface physi-/chemisorbed water, vacancy oxygen, and lattice oxygen.6 The ratio of vacancy oxygen and lattice oxygen in CuO/HfO2 was estimated to be ~0.57, over two fold that of bare CuO (~0.21) and HfO2 (~0.18). The abundant oxygen vacancies (V0) can boost chemical adsorption and activation of CO2, benefitting the ECR.

Raman spectroscopy was used to detect the local structure of CuO/HfO2. As illustrated in Fig. 1c, a typical A2g band at ~295.6 and two Bg modes at 345.2 and 626.7 cm−1 are observed for neat CuO.18 The band at 295.6 cm−1 shifted to lower value of 291.4 cm−1 for CuO/HfO2, indicating prominent interaction between the metal oxides. The peaks at ~132.6, 259.7, 383.1, 500.2, 579.4, and 670.9 cm−1 could be assigned to the A2g modes of HfO2, while the vibrations found at 163.1, 242.3, 323.3, 335.2, 395.4, 548.3, and 641.3 cm−1 are attributed to the Bg modes of monoclinic HfO2.18 The two characteristic phonon frequencies at 146.1 and 520.2 cm−1 may correspond to the IR active F23u (F16) mode and 3Ig2 (F2g) band of CuO.6 Temperature-programmed reduction by hydrogen (H2-TPR) showed two peaks at ~210.5 and 252.3 °C for CuO/HfO2 (Fig. S5a), corresponding to the respective reduction of Cu2+ to Cu+ and Cu+ to Cu. CuO/HfO2 exhibited these remarkably lower TPR temperatures compared with bare CuO due to hydrogen spillover to the cupric oxide at the composite interface. This implies that HfO2 in proximity can help reduce CuO, in the composite. By ESR spectroscopy, CuO/HfO2 was found to display a drastically more intense symmetric pair of peaks than pure CuO with a g signal at 2.00 associated with trapped unpaired electrons by oxygen vacancies via adsorbed oxygen species from air (Fig. 1d), in agreement with the XPS results.18 V0-rich surfaces of CuO/HfO2 favor CO2 adsorption and activation and also provide strong binding affinities to *CO and *CO2H, but weak affinity to *CH2, thus promoting catalytic turnover and the formation of CH4.20 Indeed, the CO2 adsorption capacity of CuO/HfO2 is two times that of pure CuO (Fig. 5b). The higher CO2 uptake may be associated with the presence of more V0 (with abundant localized electrons) on CuO, a slightly larger surface area, and also the incorporation of HfO2 with Lewis basic sites. The enhanced CO2 adsorption facilitates enrichment of CO2 on the local surface of the cathode and conduccively accelerates catalytic turnover frequency.

Microstructural characterization by scanning electron microscopy (SEM) (Fig. S6a–e) and transmission electron microscopy (TEM) (Figs. 2a and S6f) showed that the as-prepared CuO/HfO2 manifests a plate-like morphology possessing sizes of 200–400 nm with rough surfaces. Energy-dispersive X-ray spectroscopy (EDS) elemental maps (Fig. 2b–d) confirmed the presence and homogeneous dispersions of Hf, Cu, and O elements across the sample. High-resolution TEM observation and fast Fourier transformation (FFT) revealed that CuO and HfO2 are highly crystalline with ordered lattice fringes (Fig. 2e–i). The metal oxides are in close contact with large interface areas.

The inherent properties of CuO/HfO2 for ECR were first explored in a gas-tight H-type cell containing 0.1 M KHCO3 electrolyte with continuous CO2 bubbling at ambient temperature and pressure.6 The constitution of the gaseous and liquid products was monitored by gas chromatography (GC) and nuclear magnetic resonance (1H NMR) spectroscopy, respectively. Linear sweep voltammetry (LSV) test showed larger reduction currents under a CO2 environment than in an Ar atmosphere throughout the scanned potential range from 0 to −1.4 V versus reversible hydrogen electrode (vs. RHE), all the following potentials are presented relative to the RHE scale (Fig. 3a), indicating the occurrence of CO2 reduction. To study the origin of ECR reactivity, the catalytic performances over CuO/HfO2 with different Cu-to-Hf molar ratios were investigated. All catalysts were found to display a similar rough surface morphology and comparable average sizes, eliminating the influence of morphology and size on ECR activity (Fig. S6). The faradaic efficiency (FE) toward CH4 formation increased with improving HfO2 content from 2:1 (Cu-to-Hf) reaching a maximum at 3:2 (Figs. 3b and S7). Further increasing HfO2 amount caused a drop of ECR activity plausibly due to less
exposed active sites of Cu. Interestingly, we found that the trend of C₂H₄ FE fits well with the alteration of Cu'. Such a finding is in good agreement with prior observations.¹¹⁻²² The existence of Cu' could effectively decrease the energy barrier of *CO dimerization, in favor of C₂H₄ formation. Reduction products including CO, HCOOH, CH₄, and C₂H₄ together with H₂ were produced from −0.8 to −1.3 V for CuO and CuO/HfO₂, while only small amounts of HCOOH were generated on HfO₂ (Figs. 3c and S8). At potentials ≥−0.9 V, ECR mainly produces C₁ compounds of CO and HCOOH whilst the formation of C₂H₄ begins to dominate at applied bias from −1.0 to −1.2 V, which is likely due to the generation of more CO and higher *CO coverage. At more negative potentials, larger amounts of protons are formed, resulting in boosted protonation of *CO to CH₄. The FE toward C₂H₄ generation exhibits a volcano-type correlation with the increase of overpotential, reaching the highest value at −1.1 V. Notably, throughout the applied voltages, CuO/HfO₂ invariably exceeds CuO in terms of both C₂H₄ FE and overall ECR FE. This emphasizes the significance of HfO₂ in combating the HER and also accelerating the coupling of adsorbed *CO to yield C₂H₄. Particularly, CuO/HfO₂ delivers an average overall CO₂ reduction FE of 68.6% and a C₂H₄ FE of 48.7%, about 2 and 2.5 times that of individual CuO, respectively.

The partial C₂H₄ geometric current density and C₂H₄ production rate of CuO₃/HfO₂ are ~5.7 mA cm⁻² and 14 μmol mg⁻¹ h⁻¹, approximately 2.4 and 2.5 times that of bare CuO (Fig. S9a and b). Also, CuO/HfO₂ affords superior C₂H₄ selectivity (FEₐ = 0.7) compared with bare CuO over a wide voltage range from −0.8 to −1.2 V (Fig. S9c). We further estimated the C₂H₄ cathodic energy efficiency (EE) based on the C₂H₄ FE and the ratio of the thermodynamics of the reaction over cell voltage (see ESI). CuO/HfO₂ delivers a maximal C₂H₄ EE of 27.3 ± 0.7% at a current density of 11 ± 0.9 mA cm⁻² (Fig. S9d). Remarkably, both FE and EE toward C₂H₄ formation over CuO₃/HfO₂ surpass many prior reported Cu-based electrocatalysts under similar or larger overpotentials (Fig. S10 and Table S2). Alternate electrolysis cycling measurements between Ar- and CO₂-saturated electrolytes disclosed that the yield of C₂H₄ was maintained for at least four continuous cycles (Fig. S11). This also supports that the evolved C₂H₄ stemmed from the feed gas CO₂. Equally importantly, the CuO₃/HfO₂ catalysts present nearly unchanged current density and FE for C₂H₄ production even after 12 h of electrolysis at −1.1 V, indicating its long-term stability (Fig. 3d). Post characterization by XPS (Fig. S12), SEM (Fig. S13a), and TEM (Fig. S13b) showed that the surface concentration of Cu', morphological size of CuO/HfO₂ were maintained after 1 h of polarization, mirroring its good stability due to the strong interplay between HfO₂ and CuO.

To investigate the role of the CuO/HfO₂ interface, we attempted to regulate the interfacial structure by manipulation of synthetic conditions including the feeding sequence of metal precursors. It was found that a cascade addition of the two metal precursors all led to a substantial drop of C₂H₄ FE (Table S3). Similarly, a physical mixture of CuO and HfO₂ with equivalent metal oxides also exhibited lower CO₂ reduction activity compared to CuO/HfO₂ (Fig. S14). In all cases, the accessible CuO/HfO₂ interfaces with exposed copper sites were markedly reduced, which accounted for the decreased ECR performance. Therefore, we infer that engineering the interface of CuO/HfO₂ to yield and stabilize Cu' is crucial to promoting the CO₂-to-C₂H₄ conversion.

The Tafel slope of CuO/HfO₂ was calculated to be 154.5 mV dec⁻¹ (Fig. S15a), smaller than that of pure CuO (164.3 mV dec⁻¹), indicating favourable kinetics for ECR over the composite catalyst. Alternatively, Nyquist plot analysis (Fig. S15b) showed lower charge transfer resistance for CuO/HfO₂ compared to pure CuO and HfO₂, reflecting faster interfacial charge transfer between the working electrode and reactants in the electrolyte to facilitate the CO₂ conversion. In addition, CuO/HfO₂ exhibited a slightly larger electrochemical active surface area (derived from measurement of double layer capacitance) than pure CuO and HfO₂ (Fig. S16), conducive to the ECR. We further performed ECR using a three-compartment flow cell electrolyzer with gas-diffusion layers to circumvent the issue of low solubility of CO₂ in aqueous electrolytes. As illustrated in Figs. 3e and S17, the Cu₂H₄ FE was further improved to 62.6 ± 1.3% with a total ECR FE of up to 84.9 ± 0.3% at a geometric current density of 300 mA cm⁻² in 1 M KOH solution, comparable to
many previous reported Cu-based materials in flow cells (Table S4). This is in stark contrast to pure CuO with a C/H$_2$O of 11.6 ± 1.6% and overall ECR FE of 34.7 ± 0.5%.

We performed CO$_2$ and CO-TPD measurements to gain a mechanical understanding of the enhanced activity. CuO$_2$/HfO$_2$ was observed to exhibit a substantially higher CO$_2$ chemical desorption peak (412.1 °C) than pure CuO (252.5 °C) (Fig. S18a), implying larger CO$_2$ binding strength at the interface of CuO and HfO$_2$. Similarly, the CO desorption peak for CuO$_2$/HfO$_2$ approaches 354.4 °C exceeding that of 284.9 °C for CuO, as shown in Fig. S18b, suggesting a much stronger CO binding energy on the metal oxide composite. As a consequence, we conclude that the introduction of HfO$_2$ greatly enhanced the CO$_2$ and CO adsorption on CuO$_2$ surface. The association of strong CO binding is believed to be the active sites for C=C coupling. Moreover, we conducted CO electroreduction measurements in H-cells with 0.1 M KOH as cathodic electrolyte (Fig. S19). CuO$_2$/HfO$_2$ started to form C$_2$H$_4$ at ~0.3 V and attained a maximal C$_2$H$_4$ FE of 50.5 ± 1.7% (at ~0.4 V), whereas bare CuO did not yield C$_2$H$_4$ at potentials more positive than ~0.4 V. This further validates that the CuO$_2$/HfO$_2$ interface can efficiently catalyze C=C coupling reactions at low overpotentials. Furthermore, operando Raman spectroscopy measurements were carried out to detect reaction intermediates and catalyst structural alteration during CO$_2$ reduction. In contrast to absence of peaks for pure CuO after 10 min of CO$_2$ electrolysis (Fig. 3f), a prominent band located at ~299.7 cm$^{-1}$ appeared on CuO$_2$/HfO$_2$ which became gradually stronger with polarization time (Fig. 3g). This peak is associated with the frustrated rotation of *CO bound to Cu$_2$O in an atop geometry, which locally protected Cu$^+$ sites against further reduction. This provides an evidence that the incorporated Hf species facilitate strong *CO binding and high *CO coverage, contributing to the enhanced C=C coupling activity. Bader charge analysis by density functional theory calculations showed that the oxidation states of some Cu atoms at the CuO$_2$/HfO$_2$ interface fall between that of Cu$_2$O and CuO (Fig. 3h), illustrating that the interfacial HfO$_2$ cluster altered the oxidation state of adjacent Cu atoms in CuO toward that of Cu$_2$O. This is in accordance with the above XRD, XPS, and TPR results, verifying the existence of Cu$^+$ in CuO$_2$/HfO$_2$, and that HfO$_2$ plays a central role in stabilizing Cu$^+$. In summary, we have demonstrated that tuning of the CuO$_2$/HfO$_2$ interface can greatly boost CO$_2$ adsorption and binding of *CO, thus facilitating tandem dimerization and protonation to produce C$_2$H$_4$ via ECR. The designed metal oxide composite imparted a remarkable FE toward C$_2$H$_4$ formation, reaching 62.6 ± 1.3%, and with an overall CO$_2$ reduction FE of 84.9 ± 0.3% at a high current density of 300 mA cm$^{-2}$, over fivefold that of pure CuO and also outperforming prior reported Cu-based electrocatalysts. Tailoring the level of HfO$_2$ incorporation enables fine-tuning of the ECR activity and also impedes the competing HER. The activity of the catalyst maintains good stability even after consecutive polarization for 12 h. The existence of Cu$^+$ species was confirmed by XRD, XPS, TPR, and Bader charge analysis. Operando Raman spectroscopy measurements corroborate that the introduction of HfO$_2$ significantly strengthened *CO binding and coverage, thus improving C=C coupling activity. This work offers a simple and effective avenue to enhancing the ECR to yield C$_2$H$_4$.

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Conflicts of interest
The authors declare no conflicts of interest.

Notes and references