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Enhancing electrocatalytic CO₂ reduction via engineering substrate–cluster interaction†

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Cu clusters exhibit exceptional performance in the electrocatalytic carbon dioxide reduction reaction (CO₂RR) due to their tunable size. Using first-principles calculations, we systematically investigate the CO₂RR on small Cu_{*n*} clusters (*n* = 3, 8, 13) anchored on a T'-WTe₂ substrate, denoted as Cu_{*n*}@T'-WTe₂. Given that the hydrogen evolution reaction (HER) often competes with the CO₂RR, we further investigated the competition between the CO₂RR and HER. Our results show that Cu_{*n*}@T'-WTe₂ outperforms pure Cu_{*n*} clusters as catalysts, with enhanced CO₂RR activity. The CO₂RR performance of Cu_{*n*}@T'-WTe₂ enhances with increasing cluster size, and surpasses the HER activity in Cu₁₃@T'-WTe₂. This enhancement stems from the substrate–cluster interactions, where the buckled “non-uniform surface” of T'-WTe₂ deforms the larger Cu₁₃ cluster, optimizing the CO₂RR efficiency. We propose a potential strategy for WTe₂-supported Cu clusters to boost CO₂RR while suppressing HER by leveraging substrate-supported Cu clusters.

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1. Introduction

The accumulation of greenhouse gases, particularly carbon dioxide (CO₂), drives global warming and poses significant environmental and energy challenges.^{1,2} To address rising energy demands and mitigate CO₂ emissions, researchers have explored various strategies to convert CO₂ into valuable chemicals and feedstocks,³ including chemical reforming,^{4,5} bioconversion,⁶ photocatalysis,^{7,8} and electrocatalysis.^{9,10} Among them, the electrochemical CO₂ reduction reaction (CO₂RR) stands out as a promising approach, transforming CO₂ into valuable products^{8,10–12} like methane (CH₄),^{6,13} formic acid (HCOOH),¹⁴ and methanol (CH₃OH).^{15,16} However, the CO₂RR faces challenges such as low efficiency and poor product selectivity^{4,9,17} exacerbated by the competing hydrogen evolution reaction (HER), which significantly reduces the performance of the CO₂RR.¹⁸

To overcome these limitations, significant efforts have focused on designing efficient electrocatalysts that activate inert CO₂ molecules while suppressing the competitive HER. Various systems, including metals,^{19,20} metal oxides,^{21,22} clusters,²³ carbon-based materials,^{24,25} and metal–organic frameworks,^{26,27} have been explored. Among them, clusters, in particular Cu clusters, demonstrate excellent CO₂RR catalytic

performance.^{28,29} When supported on substrates, the synergistic interaction between the substrate and cluster significantly influences the CO₂RR efficiency.³⁰ Thus, optimizing the substrate–cluster pairing is critical to maximizing the CO₂RR activity and minimizing HER interference.

In this study, we employ first-principles calculations to examine the CO₂RR performance of Cu_{*n*} clusters (*n* = 3, 8, 13) anchored on a T'-WTe₂ substrate denoted as Cu_{*n*}@WTe₂.^{31–33} Compared to unsupported Cu_{*n*} (Cu₃, Cu₈, and Cu₁₃),^{28,34–36} our findings reveal that the T'-WTe₂ substrate reduces the absolute limiting potential for the CO₂RR process ($|U_L|$),³⁷ while inhibiting the competitive HER. This improvement is attributed to the strong distortion of larger Cu₁₃ clusters by the buckled T'-WTe₂ surface, facilitating rapid charge transfer between the cluster and substrate. Our work provides an effective approach for enhancing CO₂RR efficiency *via* engineering substrate–cluster interactions.

2. Computational methods

Spin-polarized density functional theory (DFT) calculations were carried out using the Vienna ab initio simulation package (VASP).^{38,39} The projector-augmented-wave (PAW) method was employed to treat the core wave functions.⁴⁰ The generalized gradient approximation (GGA) in the Perdew–Burke–Ernzerhof (PBE) form is adopted.^{41,42} Long-range van der Waals (vdW) interaction was corrected using the DFT-D3 scheme,⁴³ and a vacuum space exceeding 20 Å was used to minimize periodic interactions. The 3 × 3 × 1 Monkhorst–Pack *k*-points in the Brillouin zone are sampled for structural optimizations, and

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dense $6 \times 6 \times 1$ k -meshes are set for the density of states (DOS) calculations for T'-WTe₂. $15 \text{ \AA} \times 15 \text{ \AA} \times 15 \text{ \AA}$ cubic cells are used to optimize the isolated Cu₃, Cu₈ and Cu₁₃ clusters before loading on the WTe₂ surfaces. The cutoff energy for the plane wave basis is 400 eV in all the calculations, and the energy and force convergence criterion are respectively set to 10^{-5} eV and 10^{-2} eV \AA^{-1} . We used VASPsol for the implicit solvation calculations.⁴⁴ Water is considered as the continuum solvent throughout, with a bulk static dielectric constant ϵ_s of 80.⁴⁵ In addition, canonical *ab initio* molecular dynamics simulations (AIMDs) with a Nosé thermostat and integrating time with the Verlet algorithm at a time step of 1 fs are employed to investigate the thermodynamic stability of the catalyst.⁴⁶

The isolated CO₂ molecule is simulated in a large cubic cell of 15 \AA in length. The adsorption energies are calculated according to the equation $E_{\text{ads}} = E_{\text{adsorbed-system}} - E_{\text{molecule}} - E_{\text{catalyst}}$, where $E_{\text{adsorbed-system}}$, E_{molecule} , and E_{catalyst} are the total energies of the catalyst with CO₂*, the isolates CO₂ molecule and Cu_{*n*}@WTe₂ ($n = 3, 8, 13$), respectively. The Bader charge, charge density difference, and DOS are calculated to clarify the interactions between the adsorbed molecule and the catalyst surface. To calculate the free energy profiles of the electrocatalytic CO₂RR, the computational electrode model (CHE) is employed.⁴⁷ The free energy change (ΔG) at each elementary step of the CO₂RR process is calculated using the equation $\Delta G = \Delta E + \Delta ZPE - T\Delta S$, where ΔE is the total energy change

calculated by DFT, ΔZPE is the zero-point energy correction through frequency analysis, and T and ΔS are the reaction temperature ($T = 298.15$ K) and the entropy value change, respectively. The limiting potential (U_L) is defined as the maximum free energy change using the relation $U_L = -\Delta G_{\text{PDS}}/e$, where ΔG_{PDS} is the maximum free energy increase in a potential determining step (PDS). In addition, we utilized the post-processing functionalities provided by qvasp and VASPKIT to analyze the computational results.⁴⁸

For isolated Cu_{*n*} clusters, our calculations show finite magnetic moments ($1\mu_B$ for Cu₃, $0\mu_B$ for Cu₈, and $5\mu_B$ for Cu₁₃), in line with previous data.^{49,50} However, when supported on the T'-WTe₂ substrate, the whole system becomes nonmagnetic. The charge transfer between the clusters and substrate fully quenches the magnetism.

3. Results and discussion

3.1. Structural models of Cu_{*n*} ($n = 3, 8, 13$) clusters, CO₂ adsorption on Cu_{*n*} and CO₂RR on Cu_{*n*}

The most stable structures of Cu₃, Cu₈, and Cu₁₃ are an equilateral triangle geometry with C_{2v} symmetry,³⁴ a tetragonal crystal with D_{2d} symmetry,³⁶ and an icosahedron geometry with I_h symmetry (see Fig. 1a–c),^{35,51} respectively. The calculated Cu–Cu bond lengths ($L_{\text{Cu–Cu}}$) are 2.34 \AA for Cu₃, 2.30–2.50 \AA for Cu₈, and 2.53 \AA for Cu₁₃, which agree well with previously reported values.^{36,49,50,52}

We first examine CO₂ adsorption on Cu_{*n*} ($n = 3, 8, 13$) clusters. The most stable adsorption configurations are depicted in Fig. 1d–f, revealing a bent CO₂ geometry on all Cu_{*n*} clusters, which indicates effective activation of the CO₂ molecule. For the CO₂RR, CH₄ is the sole product across all cluster sizes; however, the potential-determining step (PDS) varies with cluster size, and the overpotential increases as the cluster size grows (see Table 1). The calculated free energy profile and the corresponding reaction intermediates along the most favorable CO₂RR pathway are provided in the ESI† (see Fig. S1 and S2). Additionally, we further investigate the HER on the Cu_{*n*} cluster (Fig. 1g–i). A comparison of U_L between CO₂RR and HER, presented in Table 1, shows that the HER suppresses the CO₂RR on all pure Cu_{*n*} clusters (see Fig. S13, ESI†).

3.2. Geometric structures of T'-WTe₂

To investigate whether substrate selection can enhance CO₂RR performance, we build on our prior findings identifying T'-WTe₂ as an effective substrate that could interact with clusters

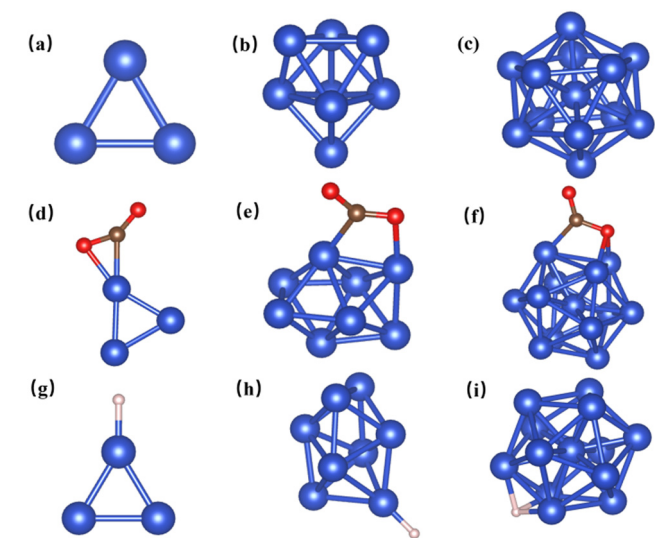


Fig. 1 (a)–(c) Structures of the pristine Cu₃, Cu₈ and Cu₁₃ clusters. (d)–(f) The most stable adsorption configurations for CO₂ on Cu₃, Cu₈, and Cu₁₃ clusters. (g)–(i) The optimized configurations for H adsorption on Cu₃, Cu₈, and Cu₁₃.

Table 1 Calculated PDS and U_L and the final product of the CO₂RR with Cu_{*n*} ($n = 3, 8, 13$) catalysts in contrast to the HER

Configurations	CO ₂ RR			HER U_L (V)
	PDS	U_L (V)	Product	
Cu ₃	*CO + e [−] + H ⁺ → *CHO	0.64	CH ₄	−0.51
Cu ₈	*OCHOH + e [−] + H ⁺ → *CHO + H ₂ O	0.85	CH ₄	0.73
Cu ₁₃	*CO + e [−] + H ⁺ → *CHO	0.89	CH ₄	−0.14

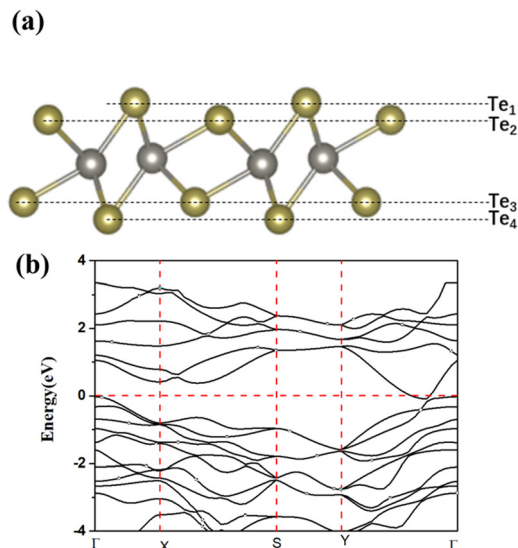


Fig. 2 (a) Schematic of the 3×2 supercell of T' - WTe_2 . W and Te atoms are denoted by grey and orange spheres, respectively. (b) Band structure for the T' - WTe_2 monolayer.

sufficiently.^{30,53} Consequently, we selected T' - WTe_2 as the substrate for loading clusters to further evaluate its CO_2RR properties.

The monoclinic metal T' phase of WTe_2 , a semimetal with no band gap (Fig. 2b), was synthesized decades ago (Fig. 2a),³² a characteristic corroborated by the calculated partial density of states (PDOS) in Fig. S6 (ESI[†]). T' - WTe_2 features three atomic layers, with nonequivalent top (Te_1 and Te_2) and bottom (Te_3 and Te_4) Te layers. The Te_1 atom sits higher than Te_2 in

the top layer, forming what we term as a 'nonuniform surface',³³ with bond lengths of 2.72 Å (L_{Te_2-W}) and 2.83 Å (L_{Te_1-W}).

3.3. CO_2 adsorption and electroreduction for $Cu_n@T'-WTe_2$ ($n = 3, 8, 13$)

Firstly, we investigate the adsorption of Cu_n ($n = 3, 8, 13$) clusters on the T' - WTe_2 substrate, with all optimized configurations presented in Fig. S3–S5 (ESI[†]). The most stable structures for $Cu_3@T'-WTe_2$ (Fig. S3b, ESI[†]), $Cu_8@T'-WTe_2$ (Fig. S4h, ESI[†]), and $Cu_{13}@T'-WTe_2$ (Fig. S5d, ESI[†]) are highlighted, in Fig. 3 for further studying the CO_2RR . Bader charge analysis (Table S1, ESI[†]) reveals electron transfers of 0.28e, 0.32e and 0.18e from Cu_3 , Cu_8 , and Cu_{13} to T' - WTe_2 , respectively, indicating significant substrate–cluster interactions, further evidenced by orbital hybridization in the PDOS (Fig. S7, ESI[†]). As noted in Section 2, while isolated Cu_n clusters exhibit size-dependent magnetism, the interaction with the T' - WTe_2 substrate leads to complete spin quenching. The AIMD simulation at 500 K over 5ps (Fig. S11, ESI[†]) shows no structural degradation, confirming the excellent thermal stability of the $Cu_n@T'-WTe_2$ catalyst under ambient conditions.

To assess the substrate's role in the CO_2RR performance, we studied CO_2 adsorption on the $Cu_3@T'-WTe_2$, $Cu_8@T'-WTe_2$, and $Cu_{13}@T'-WTe_2$ surfaces. Various adsorption configurations of CO_2 on the catalyst surfaces are considered as shown in Fig. S8 (ESI[†]). Strong adsorption energy typically elongates the C–O bond length in the adsorbed CO_2 molecule.^{17,54,55} Fig. 3 presents the most favorable sites for CO_2 adsorption, showing L_{C-O} extended to 1.22 Å and 1.88 Å (Fig. 3a), 1.25 Å and 1.28 Å (Fig. 3d), and 1.26 Å (Fig. 3g) for the $Cu_3@T'-WTe_2$,

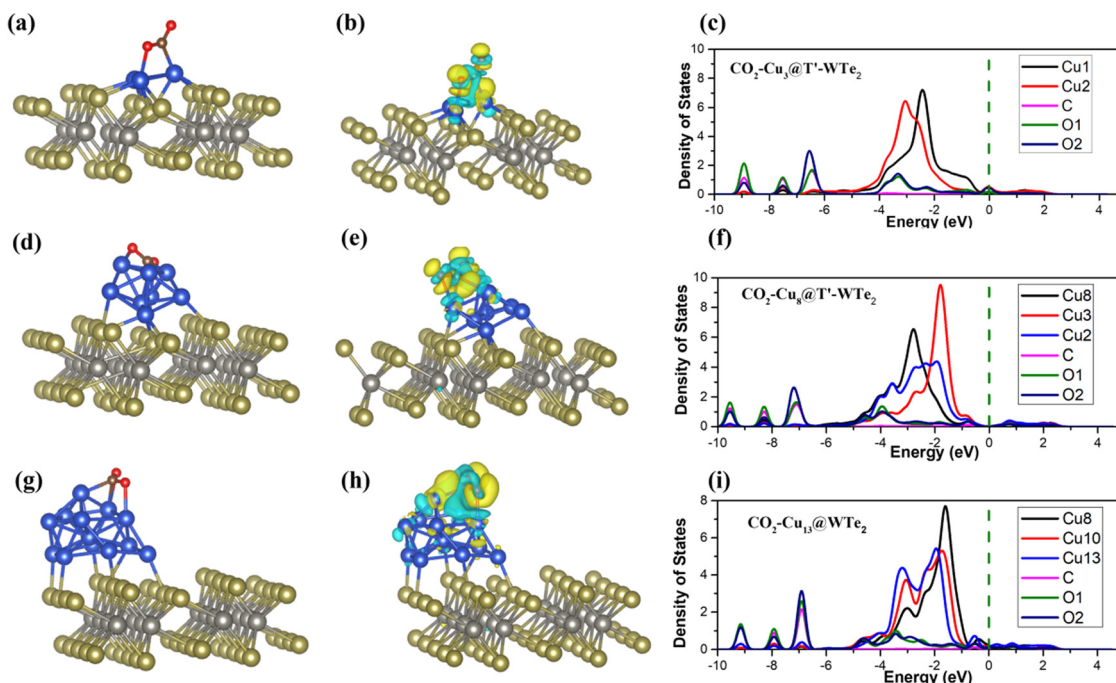
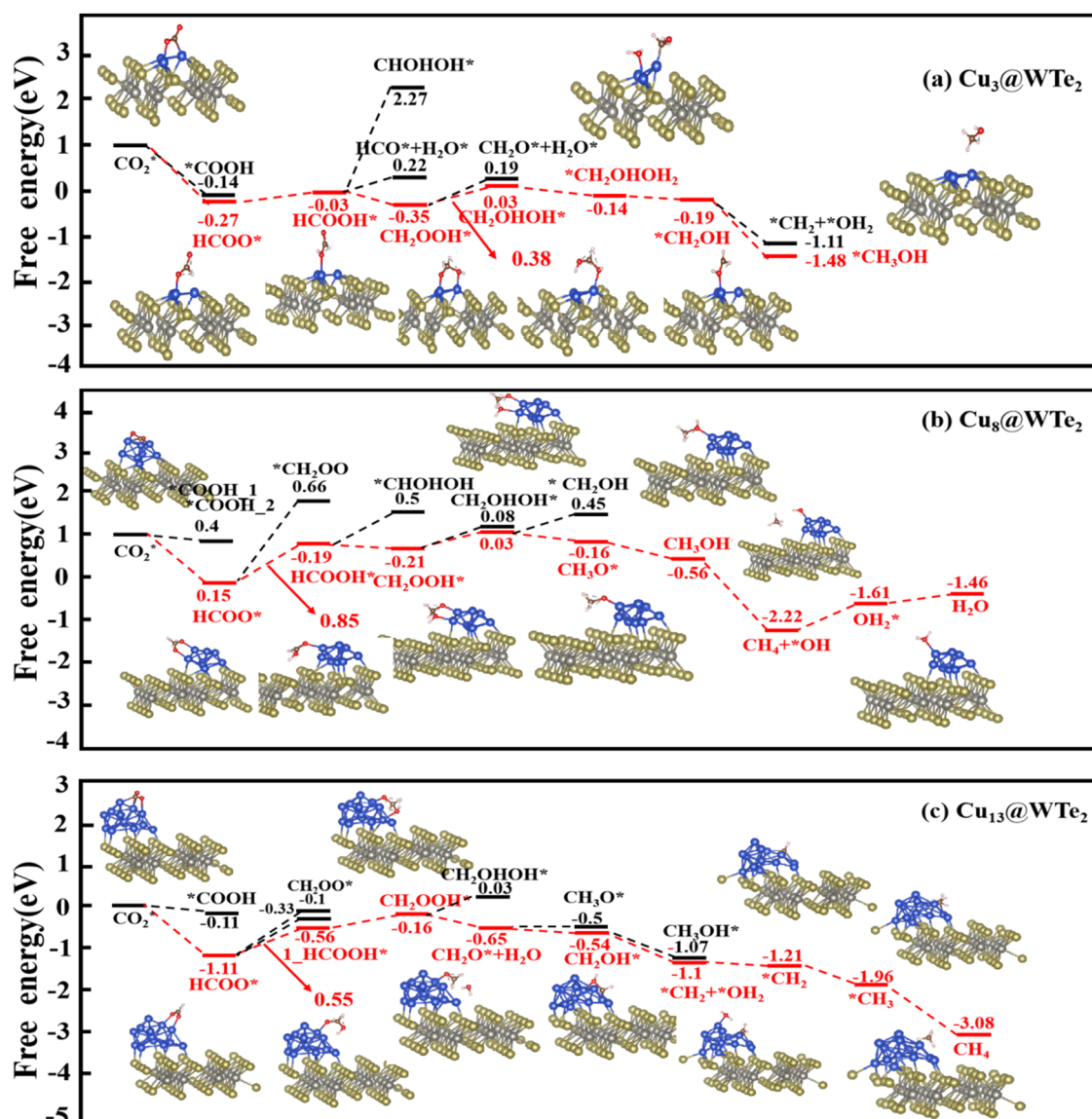


Fig. 3 The most stable adsorption configurations, the isosurface of the charge density difference with an isovalue of 0.003 \AA^{-3} , and the PDOS for CO_2 on $Cu_3@WTe_2$: (a)–(c), $Cu_8@WTe_2$ (d)–(f) and $Cu_{13}@WTe_2$ (g)–(i). The blue (yellow) wireframes denote the loss (gain) of electrons with the isosurface values set as 0.003 \AA^{-3} . The Fermi level is assigned at 0 eV.

Adsorption configurations	$E_{\text{ads-free}}$ (eV)	$\angle \text{OCO}$	$L_{\text{C-O}}$ (Å)	Δq (e)
CO ₂ -Cu ₃ @WTe ₂	-0.10	134.2°	1.22; 1.28	0.62
CO ₂ -Cu ₈ @WTe ₂	-0.33	130.6°	1.25; 1.28	0.79
CO ₂ -Cu ₁₃ @WTe ₂	0.02	132.3°	1.26	0.74

reveals orbital hybridization and charge transfer between Cu, C, and O atoms, underscoring the strong interaction between the CO₂ molecules and the Cu_{*n*}@T'-WTe₂ catalysts.^{11,56,57} The charge density difference (see Fig. 3) and the Bader charge analysis (Table 2) further confirm electron donation from Cu_{*n*}@WTe₂ to the CO₂ molecule (around 0.62e–0.79e). The broadly dispersed PDOS peaks for C and O relative to isolated CO₂ molecules (Fig. S9, ESI[†]) and the hybridization with Cu atoms also support the strong interaction between CO₂ and Cu_{*n*}.

We next explore the CO₂RR pathways on Cu_{*n*}@WTe₂. Fig. 4 illustrates the calculated free energy profile for the most favorable CO₂RR pathways on Cu₃@WTe₂, Cu₈@WTe₂, and Cu₁₃@WTe₂, with the corresponding optimal reaction configurations shown in Fig. S10 (ESI[†]). For CO₂-Cu₃@WTe₂, the



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Table 3 The calculated U_L ($|U_L|$), HCOO intermediate adsorption (ΔG_{HCOO}^*) and final product of CO₂RR, and the H* intermediate adsorption (ΔG_{H}^*) of the HER with Cu_n@WTe₂ ($n = 3, 8, 13$) catalysts

Configurations	CO ₂ RR			HER	
	$ U_L $ (V)	ΔG_{HCOO}^* (eV)	Product	$ U_L $ (V)	ΔG_{H}^* (eV)
Cu ₃ @WTe ₂	0.38	−0.27	CH ₃ OH	0.10	0.10
Cu ₈ @WTe ₂	0.86	−1.04	CH ₄	0.05	−0.05
Cu ₁₃ @WTe ₂	0.55	−1.11	CH ₄	0.85	−0.85

initial H⁺ and e[−] pair attacks the carbon atom of CO₂, forming HCOO* with a free energy change of −0.27 eV. Subsequent hydrogenation yields HCOOH*, followed by an exothermic step forming CH₂OOH* as shown in Fig. 4a, which is energetically more preferred than the formation of CHOH* or HCO* + H₂O*. Further hydrogenation of CH₂OOH* favors CH₂OH* ($\Delta G < 0$) over CH₂O* + H₂O*. Two subsequent additions of the H⁺ and e[−] pair will attack the O atom, releasing the H₂O molecule and leaving *CH₂OH, which undergoes successive hydrogenation steps to produce CH₃OH molecules. Overall, the PDS is the formation of CH₂OH* from CH₂OOH* with a U_L of −0.38 V.

For the Cu₈@WTe₂ and Cu₁₃@WTe₂ surface, the initial step of the CO₂RR is the formation of HCOO*, followed by hydrogenation of HCOO* to form HCOOH* (see Fig. 4b and c), which is more energetically favorable than that of CH₂OOH*. HCOOH* then converts to CH₂OOH*. On Cu₈@WTe₂, CH₂OOH* after hydrogenation will transform into CH₂O* + *OH₂, proceeding to CH₃OH* and ultimately producing CH₄. On Cu₁₃@WTe₂, CH₂OOH will be further hydrogenated to CH₂O* with H₂O release, followed by hydrogenation to *CH₄ with the final release of the CH₄ molecule. The PDS for both the Cu₈@WTe₂ and Cu₁₃@WTe₂ systems is HCOO* → HCOOH*, with U_L values of −0.85 V and −0.55 V, respectively. The free energy values ($G(T)$) for these pathways are detailed in Table S3 (ESI†).

The analysis reveals that Cu₃@WTe₂, Cu₈@WTe₂, and Cu₁₃@WTe₂ all exhibit robust CO₂RR activity. On Cu₃@WTe₂, CO₂RR proceeds *via* a 6e[−] charge transfer pathway, yielding CH₃OH, whereas Cu₈@WTe₂ and Cu₁₃@WTe₂ favor an 8e[−] charge transfer reaction pathway, producing CH₄ as the primary product. Comparison of the overpotentials with pure Cu_n clusters (Table S2, ESI†) shows that Cu_n on the T'-WTe₂ substrate outperforms their standalone counterparts, with lower $|U_L|$ values indicating enhanced CO₂RR efficiency. Specifically, $|U_L|$ for Cu₃@WTe₂ is 0.38 V (vs. 0.64 V for pure Cu₃, a 0.26 V reduction), while $|U_L|$ for Cu₁₃@WTe₂ is 0.55 V (vs. 0.89 V for pure Cu₁₃, a 0.34 V reduction). This suggests that the T'-WTe₂ substrate significantly boosts the CO₂RR performance, with the enhancement scaling with Cu cluster size.

3.5. Analysis of the hydrogen evolution reaction and solvent effects

To evaluate the competing HER,¹⁸ we analyzed the HER performance on Cu_n@WTe₂ ($n = 3, 8, 13$), as detailed in Fig S12 and S14 (ESI†). In all the optimized configurations, H atoms preferentially bind to Cu clusters rather than the WTe₂ surface.

Catalytic selectivity was assessed using the difference in U_L values, *i.e.*, $|U_{\text{L}(\text{CO}_2)}| - |U_{\text{L}(\text{H}_2)}|$,³⁷ where a positive value of $|U_{\text{L}(\text{CO}_2)}| - |U_{\text{L}(\text{H}_2)}|$ indicates a poor CO₂RR selectivity over the HER. For the Cu₁₃@T'-WTe₂, the $|U_{\text{L}(\text{CO}_2)}| - |U_{\text{L}(\text{H}_2)}|$ is calculated to be −0.30 V (see Table 3), suggesting a better CO₂RR selectivity over the HER. Given that HCOO* is a critical intermediate in all CO₂RR pathways, we then considered the competition between H* and HCOO*.^{55,58–60} For the Cu₁₃@WTe₂, HCOO* formation (Fig. 4c) has a free energy change of −1.11 eV, more favorable than −0.85 eV for the HER process (see Table 3), indicating greater HCOO* stability over H*.

To further gain an in-depth understanding of the catalyst effects, we compared the DOS curves of isolated and adsorbed HCOO* intermediates on the catalyst. As shown in Fig S15 (ESI†), the 2p orbitals of O and C atoms after adsorption shift toward lower energy region near the Fermi level, with larger shifts reflecting stronger intermediate–substrate interaction, and the lower adsorption energy.^{17,61,62} Cu₁₃@WTe₂ exhibits the lowest adsorption energy (−1.11 eV) compared to −0.27 eV for Cu₃@WTe₂. This suggests that the buckled T'-WTe₂ surface enhances CO₂RR activity in the supported Cu_n nanocluster, with larger cluster size strengthening substrate–Cu interactions and boosting electrocatalytic CO₂ reduction.

Overall, Cu₁₃@WTe₂ emerges as the optimal CO₂RR electrocatalyst among the studied configurations. We further examine its electrochemical CO₂RR performance using free energy diagrams with an implicit solvation model (Fig. S16, ESI†). The PDS remains unchanged, with the U_L value shifting by only 0.09 V upon incorporating the solvation effect. These findings suggest that the electrolyte environment exerts minimal influence on the CO₂RR performance of the Cu₁₃@WTe₂ catalysts.

4. Conclusions

In conclusion, we theoretically investigate the CO₂ electrocatalytic properties on pure Cu clusters and their performance when supported on a T'-WTe₂ substrate. Our results reveal that the introduction of the WTe₂ substrate significantly reduces the CO₂RR overpotential across the system, with Cu₁₃@WTe₂ exhibiting particularly notable suppression of the competing hydrogen evolution reaction (HER). Our findings elucidate the size-dependent electrocatalytic behavior of the CO₂RR and HER across different Cu clusters while highlighting the critical role of the substrate in modulating electrochemical performance. Collectively, this work offers valuable insights and a strategic framework for designing efficient CO₂RR catalysts, paving the way for future experimental advancement in electrocatalytic systems.

Author contributions

Qian Sun: data curation, writing – original draft. Huiru Yang: revise the manuscript. Chunmei Zhang: writing – original draft, writing – review & editing. Aijun Du: revise the manuscript and

technical support. All authors contributed to the results interpretation and manuscript preparation.

Data availability

The data presented in this work is available from the corresponding author upon reasonable request.

Conflicts of interest

There is no conflict to declare.

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