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Atomically dispersed copper catalysts for highly selective CO₂ reduction†

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Support substrates play important roles in the catalysis process. Herein, atomically dispersed CuN₃ catalysts supported by two different types of zirconia (denoted as CuN₃/NC/T-ZrO₂ and CuN₃/NC/M-ZrO₂) have been rationally fabricated to uncover the influence of the support. CuN₃/NC/T-ZrO₂ exhibits outstanding performance for electrochemical CO₂ reduction towards CO at a wide range of potentials (~96%, 0.6–0.8 V vs. RHE) owing to the acidic uncoordinated Zr⁴⁺ sites of T-ZrO₂, which facilitate CO₂ accumulation, and N-doped carbon (NC), which enhances the conductivity of the catalyst. Moreover, density functional theory calculations prove that T-ZrO₂ effectively decreases the Gibbs free energy for CO₂ to CO conversion. Significantly, this study reports the effects of the substrate on the electrocatalytic CO₂RR and provides a promising strategy for tuning catalytic activity and selectivity during the process of converting CO₂ into high-value products by controlling the phase of the support for the first time.

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Introduction

As the consumption of fossil fuels increases, climate change has become a major global issue owing to sea-level rise and global warming.¹ In recent years, many efforts have been made to convert CO₂ into useful chemical feedstocks by designing and tuning appropriate catalytic active sites.² These strategies are key to reducing fossil fuel dependence. Among them, the electrochemical CO₂ reduction reaction (EC-CO₂RR) has been considered a promising route to obtain value-added products such as methane, formate, and CO.³ However, the major competitive process of the H₂ evolution reaction (HER) during the EC-CO₂RR must be suppressed.⁴ Hence, it is necessary to develop robust electrocatalysts to selectively produce target products during the EC-CO₂RR process.⁵

Atomically dispersed single metal site catalysts are a new research topic that has attracted increasing attention. These catalysts are a promising technology with tunable active sites and substrates, aiming at higher activity and selectivity during heterogeneous catalytic reactions.⁶ Additionally, Cu species, as an abundant non-noble metal, have excellent per-

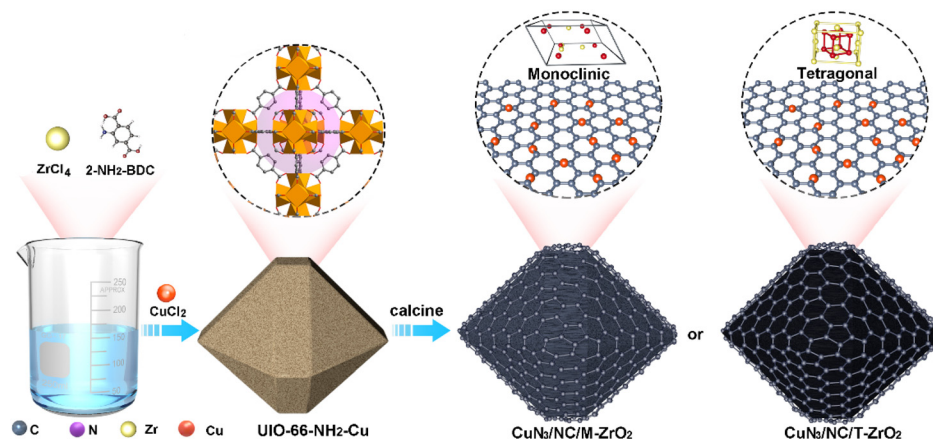
formance in catalytic systems. Some examples include electrochemical CO₂ reduction by Cu-based MOFs and Cu particles,⁷ Cu clusters for CO₂ methanation,⁸ and single Cu atoms applied to the O₂ evolution reaction.⁹ Additionally, the interaction between the catalyst and support is an important factor in the activity of catalysts.¹⁰ Zirconia is a commonly used substrate with many advantages, such as high thermal stability, good mechanical performance, and the presence of various phases with different chemical and physical characteristics.¹¹ Some of the most widely used Cu/ZrO₂ catalysts for the conversion of CO₂ include Cu and Cu oxides combined with zirconia present in monoclinic or tetragonal phases.¹²

To explore the influence of different substrates on catalytic performance, we designed two catalysts with atomically dispersed CuN₃ sites supported on zirconia with monoclinic (CuN₃/NC/M-ZrO₂) and tetragonal (CuN₃/NC/T-ZrO₂) phases. The synthetic approach has been simply divided into three steps, as illustrated in Scheme 1. There are equal Lewis and Brønsted acid centers in M-ZrO₂, and water is a Lewis base that can be concentrated by M-ZrO₂, while only the Brønsted acid sites of T-ZrO₂ suppress the HER during the EC-CO₂RR. As expected, the atomically dispersed CuN₃ sites favoured the reduction of CO₂, while the formation of strong metal–support interactions contributed to the enrichment of different reactants, resulting in the diverse catalytic activity of catalysts for the EC-CO₂RR. CuN₃/NC/T-ZrO₂ exhibits high activity for the EC-CO₂RR to produce CO with high faradaic efficiency of up to 96%, while CuN₃/NC/M-ZrO₂ exhibits negligible CO₂RR activity with H₂ as the main product.

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Scheme 1 Schematic illustration of the synthesis of atomically dispersed Cu sites supported on zirconia.

Results and discussion

Singly dispersed CuN_3 sites were formed by pyrolyzing UIO-66- NH_2 -Cu, which prevents metal from aggregating owing to coordination bonds between the Cu and $-\text{NH}_2$ groups (ESI, Fig. S1†). The powder X-ray diffraction (PXRD) patterns of $\text{CuN}_3/\text{NC}/\text{T-ZrO}_2$, $\text{CuN}_3/\text{NC}/\text{M-ZrO}_2$, and CuN_3/NC possess a broad peak around 26° assigned to the (002) peaks of defective graphitic stacking, which allows the Cu atom to be isolated on the substrate support. The absence of significant Cu peaks in the PXRD profiles also agrees with the structural interpretation (Fig. S2†). The N_2 and CO_2 adsorption isotherms reveal that $\text{CuN}_3/\text{NC}/\text{T-ZrO}_2$ exhibits better BET surface area and CO_2 uptake than $\text{CuN}_3/\text{NC}/\text{M-ZrO}_2$, indicating that $\text{CuN}_3/\text{NC}/\text{T-ZrO}_2$ possesses high CO_2 affinity that facilitates CO_2 conversion (Fig. S4 and S5†). Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images show no clear evidence of particles (Fig. 1b–d). However, high-resolution scanning transmission electron microscopy (STEM) does not exhibit particles, indicating atomically dispersed Cu sites in the structure (Fig. 1f). As is well known, singly dispersed metal sites cannot exist solely on zirconia or carbon support owing to their higher surface energy. Hence, the N-doped carbon matrix obtained *via* the pyrolysis of UIO-66- NH_2 plays an efficient role in fixing singly dispersed Cu sites through the formation of Cu–N bonds. As elemental mapping analysis shows, the homogeneous distribution of Cu, N, C, Zr, and O verifies that the Cu sites are dispersed uniformly over the substrate (Fig. 1g).

Thereafter, X-ray photoelectron spectroscopy (XPS) was performed to verify the chemical formation of $\text{CuN}_3/\text{NC}/\text{T-ZrO}_2$. The XPS spectra confirm the existence of Cu, Zr, N, O, and C. The N 1s spectrum of the catalyst exhibits three deconvoluted peaks of 398.0 eV (pyridinic-N), 399.4 eV (Cu–N), and 400.3 eV (graphitic-N). This N distribution corresponds to previous reports on singly dispersed metal site catalysts, and the pyridinic-N forms a Cu–N bond. The two main peaks in the O 1s spectrum at 529.9 and 531.3 eV are attributed to the contri-

bution of O bonded to Zr, which is consistent with the Zr 3d spectrum (Fig. 2c). The full width at half maximum of the peak in the Zr 3d spectra is approximately 1.5 eV, which verifies the existence of the tetragonal phase in the sample. The Zr $3d_{5/2}$ peak is located at 181.8 eV with a deviated value of 2.4 eV, which indicates the full oxidation of Zr^{4+} in accordance with the PXRD results. Furthermore, there is no evidence of Cu nanoparticles or clusters from the Zr 3d and O 1s spectra. The Cu $2p_{3/2}$ spectrum at 933.0 eV with a spread shape and spin–orbit deviation of 19.0 eV indicates that Cu largely differs from the metallic form and oxidation state.¹³

X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) were further employed to investigate the local atomic structure of $\text{CuN}_3/\text{NC}/\text{T-ZrO}_2$. As shown in Fig. 2e, the absorption edge of $\text{CuN}_3/\text{NC}/\text{T-ZrO}_2$ was located between that of Cu foil and CuO, indicating that the atomically dispersed Cu atoms are positively charged in $\text{CuN}_3/\text{NC}/\text{T-ZrO}_2$. This result coincided with the aforementioned XPS results. Fig. 2f shows the Fourier transform (FT) k^3 -weighted extended EXAFS spectrum of $\text{CuN}_3/\text{NC}/\text{T-ZrO}_2$. Only one dominant peak is observed at about 1.5 Å, which is attributed to the Cu–N first coordination shell. No apparent Cu–Cu coordination peaks in the FT-EXAFS spectrum of $\text{CuN}_3/\text{NC}/\text{T-ZrO}_2$ are observed, demonstrating that the Cu atoms are atomically dispersed in the support. The quantitative structural parameters of Cu in $\text{CuN}_3/\text{NC}/\text{T-ZrO}_2$ were obtained by EXAFS fitting, and the fitting curves are shown in Fig. 2g and h. The fitting results indicate that the coordination number of Cu is about 3 (Cu–N₃), and the corresponding Cu–N mean bond length is 1.95 Å. The optimized atomic structure model of the sample is shown in Fig. 2h.

The electrochemical activity towards the CO_2RR of the as-synthesized catalysts was evaluated in a three-electrode system in a high-purity CO_2 -saturated 0.5 M KHCO_3 (pH 6.8) aqueous solution. The obtained gaseous products (CO and H_2) were monitored using gas chromatography (GC), and no liquid products were detected using ^1H nuclear magnetic resonance (NMR) spectroscopy (Fig. S6†). As revealed using linear sweep

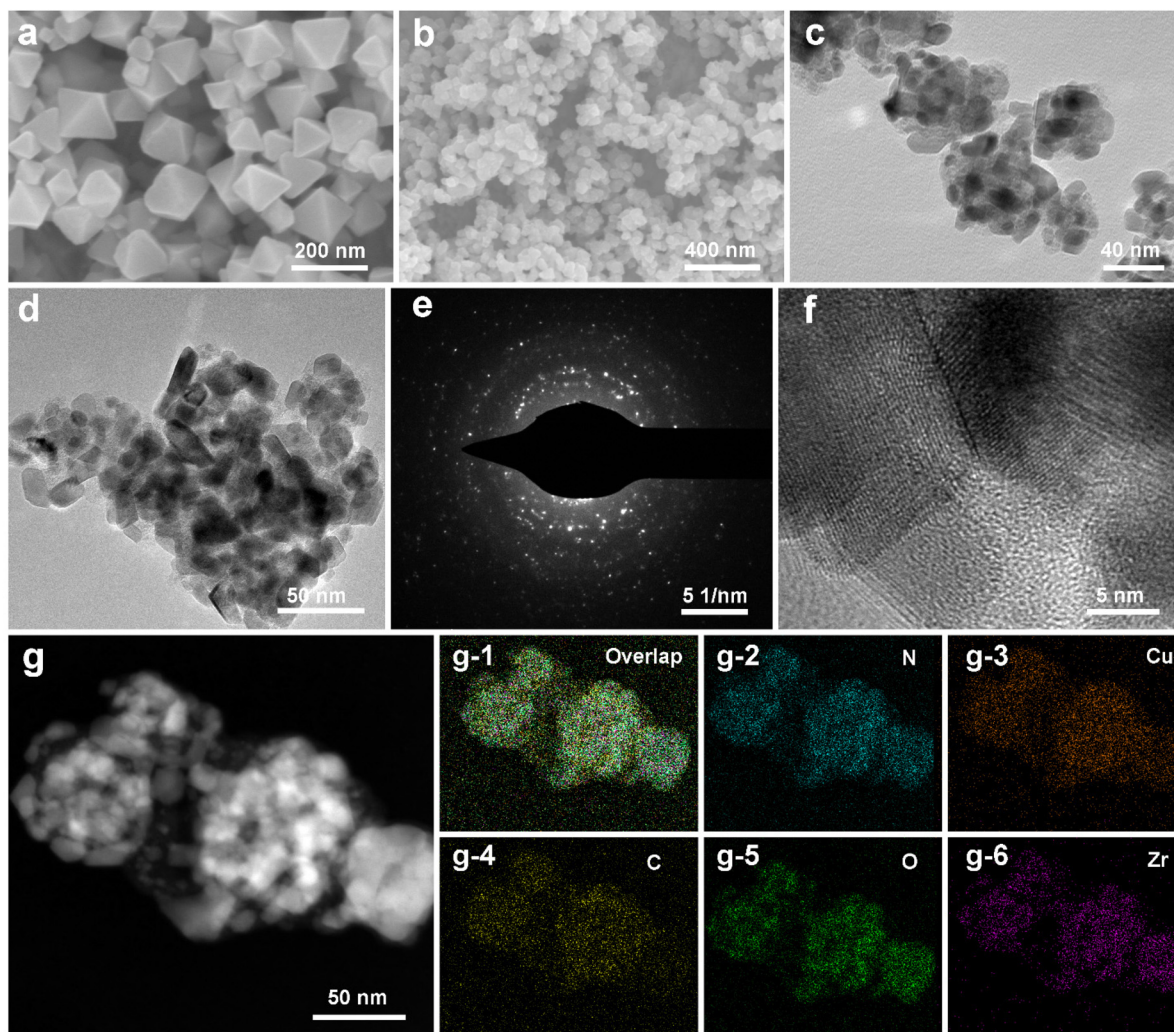


Fig. 1 (a) SEM image of Cu-UIO-66-NH₂. (b and c) SEM and TEM images of CuN₃/NC/T-ZrO₂. (d–f) TEM, selected area electron diffraction (SAED), and STEM images of CuN₃/NC/T-ZrO₂. (g) EDS elemental mapping of CuN₃/NC/T-ZrO₂.

voltammetry (Fig. 3a), CuN₃/NC/T-ZrO₂ and CuN₃/NC/M-ZrO₂ exhibit lower total current density than CuN₃/NC as ZrO₂ is an insulator. However, CuN₃/NC/T-ZrO₂ exhibits larger current densities of 5 mA cm⁻² at -0.7 V and 12 mA cm⁻² at -1.0 V (vs. RHE, Fig. 3a), indicating the importance of the N-doped carbon substrate towards facilitating electron transfer. Interestingly, the catalytic conversion of CO₂ to CO is considerably affected by the phase of the ZrO₂ substrate. In the case of T-ZrO₂, the FE_{CO} is almost 94% (higher than other Cu-based catalysts, Table S2†) at wide potential ranges of -0.6 V_{RHE} to 0.8 V_{RHE}, while M-ZrO₂ shows no activity for the CO₂RR and is more selective to the HER through the entire potential range. In contrast, when zirconia was etched by hydrofluoric acid, the catalyst retained moderate activity towards CO₂ to CO and with increasing overpotential, the HER is enhanced (Fig. 3b). The higher CO₂ to CO activity indicates the key role of the tetragonal ZrO₂ phase substrate. Compared with T-ZrO₂, in the M-ZrO₂ phase, acidic uncoordinated Zr⁴⁺ sites change to basic uncoordinated O²⁻ sites, which reject the C=O bond to reduce

the collision between C=O and the catalyst and decrease CO₂ activity. Additionally, as shown in Fig. 3d, CuN₃/NC/T-ZrO₂ has a lower Tafel slope, which indicates that electrons are transferred from the surface of CuN₃/NC/T-ZrO₂ to CO₂ molecules more easily for further reduction.¹⁴ In contrast, the significantly reduced Tafel slope for the singly dispersed CuN₃ supported by T-ZrO₂ indicates that the kinetics of electron transfer is greatly enhanced. Moreover, to evaluate the electrochemically active surface area of the three catalysts, the values of the electrochemical double-layer capacitance (*C_{dl}*) were obtained using cyclic voltammetry (Fig. 3e). The *C_{dl}* values suggest that CuN₃/NC/T-ZrO₂ (27 mF cm⁻²) possesses more active sites than CuN₃/NC/M-ZrO₂ (6 mF cm⁻²), increasing the reaction speed of the electrocatalytic process. CuN₃/NC exhibits lower selectivity, which may be attributed to the lower CO₂ uptake for subsequent reduction, which is further proof of the essentialness of the T-ZrO₂ substrate during the EC-CO₂RR to CO. More importantly, CuN₃/NC/T-ZrO₂ exhibits excellent stability for the EC-CO₂RR, retaining approximately 95% of the initial

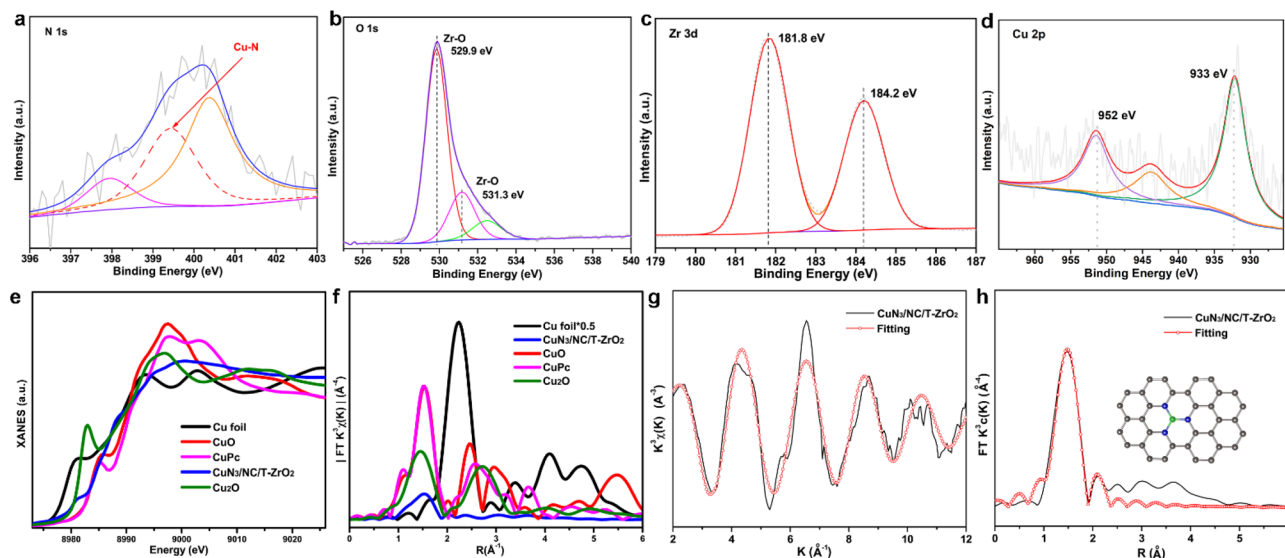


Fig. 2 (a–d) XPS spectra of Cu₃N₃/NC/T-ZrO₂: N 2p, O 1s, Zr 3d, and Cu 2p, respectively. (e) Cu K-edge data of Cu foil, CuO, CuPc, Cu₂O, and Cu₃N₃/NC/T-ZrO₂. (f) Fourier transform (FT) k^3 -weighted EXAFS profiles at the Cu k -edge. (g) Fitting curves. (h) EXAFS R space fitting curves of Cu₃N₃/NC/T-ZrO₂.

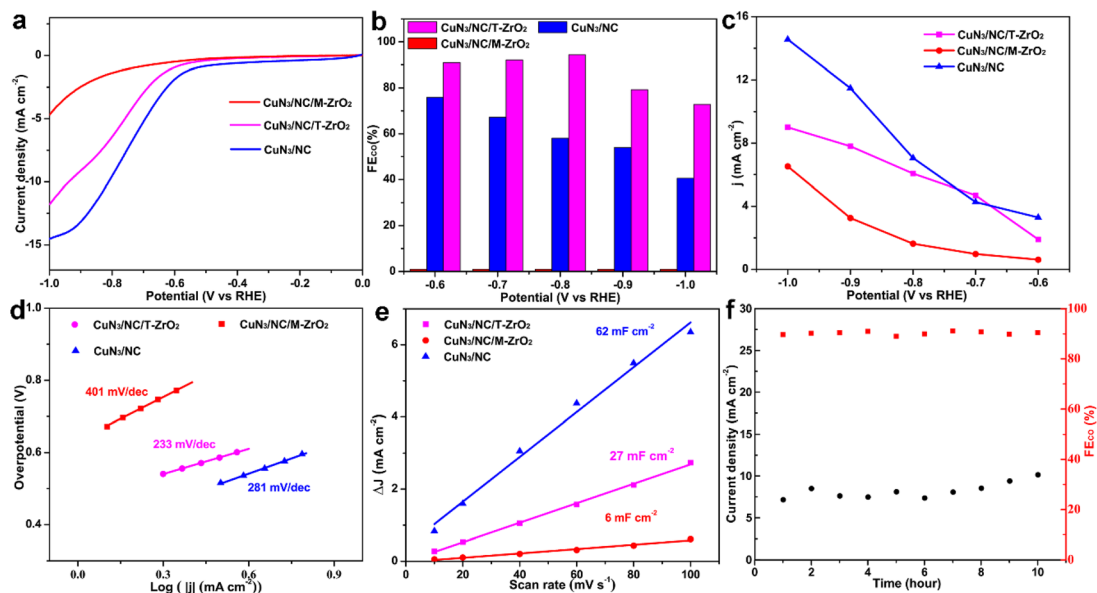


Fig. 3 Electrochemical catalytic performance of the catalysts in CO₂-saturated 0.5 M KHCO₃. (a) LSVs of Cu₃N₃/NC/T-ZrO₂, Cu₃N₃/NC/M-ZrO₂, Cu₃N₃/NC. (b) Dependence of FE_{CO} for the catalysts. (c) Current densities at different potentials. (d) Tafel slopes of the catalysts. (e) Capacitances of the electrodes calculated from linear regression of the double-layer current as a function of scan rate. (f) Long-term stability performed at -1.0 vs. RHE.

faradaic efficiency for the CO product after 10 hours of continuous electrolysis. This result indicates that as a substrate, zirconia can support the active site well owing to its outstanding mechanical performance (Fig. 3f).

To further evaluate the effects of Cu₃N₃/NC/T-ZrO₂ and Cu₃N₃/NC/M-ZrO₂ catalysts on the activity and selectivity of the CO₂RR and HER, we applied density functional theory (DFT) to calculate

the free energy and binding energy at each reaction intermediate step of the CO₂RR and HER. The most stable surfaces—the (101) face of tetragonal ZrO₂ (T-ZrO₂(101)) and (-111) of monoclinic ZrO₂ (M-ZrO₂(-111))—were employed to calculate the mechanism of the catalytic reaction (Fig. S9†).¹⁵ Fig. 4a and b show the CO₂RR to CO reaction processes on Cu₃N₃/NC/T-ZrO₂ and Cu₃N₃/NC/M-ZrO₂, in which the protonation of CO₂ to form *COOH

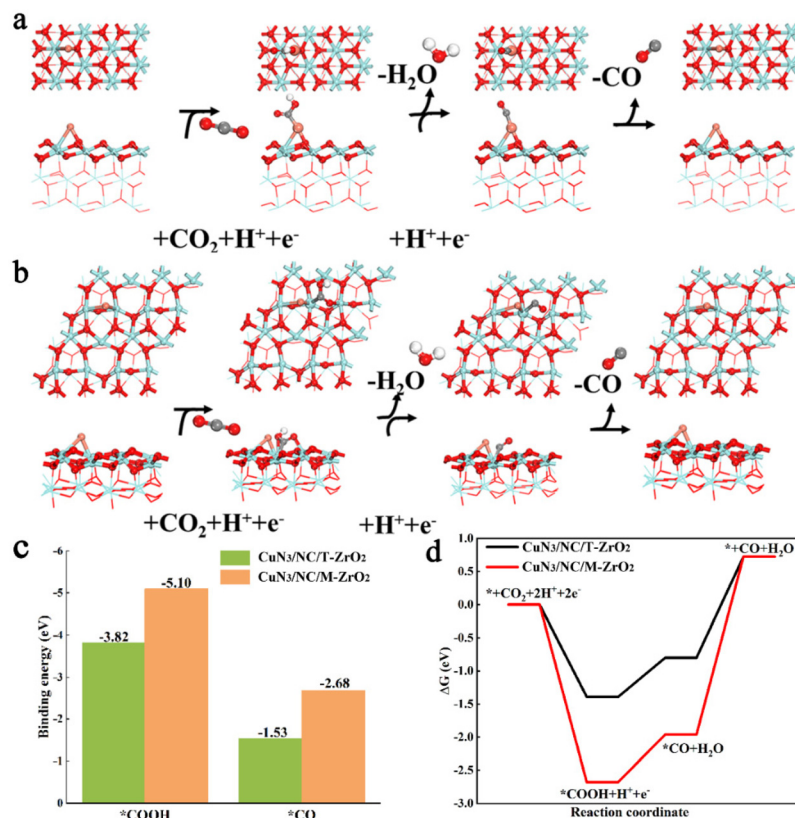


Fig. 4 (a) CO₂RR processes on CuN₃/NC/T-ZrO₂(101) and (b) CuN₃/NC/M-ZrO₂(-111). (c) Calculated binding energies (in eV) on CuN₃/NC/T-ZrO₂(101) and CuN₃/NC/M-ZrO₂(-111). (d) Calculated free energy diagrams of the CO₂RR on CuN₃/NC/T-ZrO₂(101) and CuN₃/NC/M-ZrO₂(-111).

could be identified as a potential limiting step.¹⁶ Comparing Fig. 4a and b, the adsorption sites of the CO₂RR intermediates were different in various phases. The reaction intermediates *COOH and *CO were bound at the Cu site for CuN₃/NC/T-ZrO₂, while the reaction intermediates were bound at the Zr site for CuN₃/NC/M-ZrO₂. Noticeably, the binding energies of the intermediates are significantly stronger on CuN₃/NC/M-ZrO₂ than on CuN₃/NC/T-ZrO₂ (Fig. 4c). Although the relatively strong *COOH adsorption on the catalytic sites should improve the electrocatalytic activity, the strong binding of *CO on CuN₃/NC/M-ZrO₂ (BE = -2.68 eV) makes its desorption difficult. Furthermore, DFT calculations demonstrated that the energy barriers of CuN₃/NC/M-ZrO₂ are higher than those of CuN₃/NC/T-ZrO₂, suggesting poor activity of CuN₃/NC/M-ZrO₂ for the CO₂RR. Thus, CuN₃/NC/T-ZrO₂ exhibits the best selectivity for the CO₂RR.

The free energy of *H has been identified as a descriptor of the HER,¹⁷ a competing reaction in the CO₂RR. Fig. 4d and 5 show that the free energy of *H on CuN₃/NC/M-ZrO₂ is below the free energy of *COOH, suggesting that the HER should be more favorable on CuN₃/NC/M-ZrO₂. Additionally, CuN₃/NC/T-ZrO₂ is expected to possess excellent CO selectivity owing to the weaker binding of *H compared to that of COOH*. The DFT results further demonstrate that CuN₃/NC/T-ZrO₂ favors CO formation while CuN₃/NC/M-ZrO₂ is active for H₂ evolution, which is consistent with our previously described experimental results.

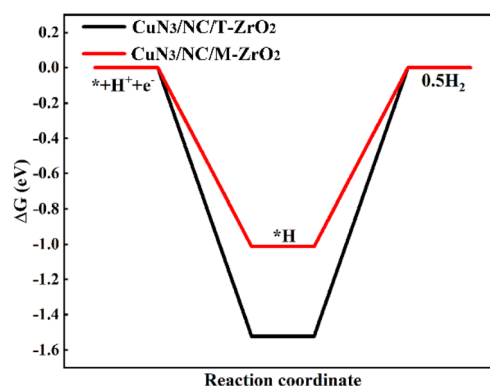


Fig. 5 DFT-calculated free energy diagrams of the HER on CuN₃/NC/T-ZrO₂(101) and CuN₃/NC/M-ZrO₂(-111) at a potential (*U*) = 0 V.

Conclusions

Herein, three EC-CO₂RR catalysts with singly dispersed Cu-N sites supported by ZrO₂ with different phases to tune the catalytic environment and enhance the selectivity for CO₂ conversion to CO have been designed and synthesized. The tetragonal phase of zirconia with acidic uncoordinated Zr⁴⁺ sites enhances C=O reduction, and N-doped carbon enhances the electrical conductivity of the catalysts. Together, the properties

of the catalysts afford the excellent ability of CO₂ to CO conversion of CuN₃/NC/T-ZrO₂. Systematic studies of CuN₃/NC/T-ZrO₂, CuN₃/NC/M-ZrO₂, and CuN₃/NC *via* experimentation and DFT calculation reveal that the acidic catalytic centre of the substrate plays a crucial factor in the generation of CO owing to its ability to concentrate CO₂ and prevent the HER. This work not only provides an in-depth understanding of the influence of the substrate during the electrocatalytic process but also provides a fundamental strategy to design promising catalysts for CO₂ to CO conversion with high selectivity and durability.

Conflicts of interest

There are no conflicts to declare.

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