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We report a theoretical analysis of the Cu electrode, modified by O impurities at the subsurface, concerning electrochemical activity of CO\textsubscript{2} reduction reaction and selectivity between CO and HCOOH evolution. On the basis of quantum mechanical simulations, we propose a novel Cu electrode modified by C impurities at the subsurface for CO\textsubscript{2} electroreduction, which has a better catalytic selectivity.

Carbon dioxide (CO\textsubscript{2}) emission causes global climate change from an environmental point of view. CO\textsubscript{2} reduction can solve these environmental problems, and at the same time it can produce economic profits due to the fact that the products of CO\textsubscript{2} reduction can serve as fuels. In order to achieve benefits from CO\textsubscript{2} reduction, we need an efficient catalyst to reduce CO\textsubscript{2} with minimal energy costs and maximal outputs. If we are able to achieve efficient electrochemical processes, many renewable electrical energy resources can be used to reduce CO\textsubscript{2}, simultaneously solving the storage issues of intermittent energies, e.g., solar, wind, geothermal, etc.\textsuperscript{1} Polycrystalline copper (Cu) electrodes have drawn a lot of attentions because they can be used to reduce CO\textsubscript{2} to hydrocarbon species.\textsuperscript{2} However, the main drawback of the Cu electrode is attributed to its very high overpotential in the order of 1 V with respect to the reversible hydrogen electrode (RHE). This is because the hydrogen evolution reaction (HER) is always dominant at low overpotential.\textsuperscript{3}

Recently, Li et al.\textsuperscript{4} reported a promising experimental technique to fabricate modified Cu electrodes by annealing Cu foil in air, followed by electrochemical reduction of the resulting Cu\textsubscript{2}O layers. With the modified Cu electrodes they can achieve a much better performance in CO\textsubscript{2} reduction to CO and HCOOH with a low overpotential of less than 0.5 V.\textsuperscript{3} Catalytic selectivity is yet another important issue. In the above experiments of Li et al.,\textsuperscript{4} the CO evolution reaction was preferred over the HCOOH evolution at a low overpotential <0.3 V, while the HCOOH evolution reaction was enhanced at an overpotential >0.3 V.

It is well-known that the Cu(211) surface is the active site, where CO\textsubscript{2} can be electrochemically reduced to a hydrocarbon at a high overpotential of ~1 V.\textsuperscript{5} However, the activity and selectivity of CO\textsubscript{2} reduction on the modified Cu electrodes are quite different. Therefore, many fundamental issues of the modified Cu electrodes are not understood yet.

In the present work, we have simulated the CO\textsubscript{2} reduction at the active sites of modified Cu electrodes to elucidate the underlying chemical mechanism in the experiment.\textsuperscript{4} We have carried out all the calculations using density functional theory (DFT). We have found that the active sites of the modified Cu electrodes are correlated with the Cu(111) surface, decorated by interstitial oxygen impurities at the subsurface. However, the Cu(211) surface is passivated by adsorbed oxygen species at the topmost surface. Moreover, we propose a novel Cu electrode, modified by interstitial carbon at the subsurface, which possesses a similar activity but a better HCOOH selectivity compared to the oxygen modified Cu electrodes.

On one hand, the modified Cu electrodes were prepared by annealing Cu foils in air and the subsequent electrochemical reduction. On the other hand, it has been found that ultrathin oxide films on surfaces of transition metals are active sites for chemical reactions.\textsuperscript{6} Therefore, we employed periodic Cu slab models, modified with interstitial oxygen impurities at the subsurface, to simulate the surface activity of the modified Cu electrodes. The Cu surface models correspond to two crystal planes, that is, Cu(111) and Cu(211), respectively. In addition, the unit cells of Cu(111) and Cu(211) surfaces are constructed based on (2×2) supercells containing five atomic layers, and (3×1) supercells containing nine atomic layers, respectively. The concentrations of interstitial oxygen impurities are in the range from one to three atoms in each unit cell, as shown in Fig.1. The Cu surfaces containing interstitial oxygen atoms are abbreviated with Cu\textsubscript{0}(111) and Cu\textsubscript{0}(211), respectively. In the Cu\textsubscript{0}(111) case, the initial sites of oxygen impurities are described using subscripts $t$ (tetrahedral), $o$ (octahedral), and $h$ (below). For the Cu\textsubscript{0}(211) case, the subscripts ($a$, $b$, and $c$) point to three different initial positions of oxygen impurities at the subsurface as shown in Fig.1. The number of subscripts corresponds to the number of O atoms for all cases.

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The stability of modified Cu(111) and Cu(211) surfaces are analyzed using formation energies of interstitial oxygen impurities calculated as follows:

\[ E_f = E_{\text{tot}} - E_{\text{Cu}} - n\mu_O \]

where \( E_{\text{tot}} \), \( E_{\text{Cu}} \), \( n \), and \( \mu_O \) correspond to the total energies of modified Cu surfaces and the pristine Cu surface, the number of interstitial impurities, and the chemical potential of oxygen atom, respectively. The chemical potential \( \mu_O \) was estimated as half the energy of a \( O_2 \) molecule, and added fluctuations in the realistic environment, \( \Delta \mu \). A negative formation energy accounts for a more stable surface.

We have calculated the free energy diagrams to analyze the electrochemical reduction processes using the computational hydrogen electrode approach:

\[ \text{H}^+ (\text{aq}) + \text{e}^- \leftrightarrow \frac{1}{2} \text{H}_2 (\text{g}) \]

the above chemical reaction is defined to be in equilibrium without applied voltage and with \( H_2 \) gas at pressure of 1 atm, at any pH values and temperatures. Therefore, the chemical potential of a proton-electron pair, that is, \( \mu (\text{H}^+) + \mu (\text{e}^-) \), is equal to \( \frac{1}{2}\mu (\text{H}_2) \) without applied external potential \( (U = 0 \text{ V}) \).

The free energy change, \( \Delta G \), of all electrochemical reactions with respect to chemical potential can be estimated using \( \Delta G = -eU \), where \( e \) is the elementary (positive) charge. In addition, the binding energies of chemical intermediates in electrochemical reductions are referred to the isolated \( CO_2 \) molecule.

All-electron Kohn-Sham equations were solved using the scheme of Linear Combination Atomic Orbitals (LCAO), as implemented in CRYSTAL09 code. Gaussian-type basis sets were used for \( H, C, O \), and \( Cu \). The difference of Cu(111) surface energies is \(-0.03 \text{ eV/Å}^2\) compared with another basis set. We have employed the Perdew-Burke-Ernzerhof (PBE) functional for the electronic exchange-correlation potential at the level of the Generalized Gradient Approximation (GGA).

The hybrid PBE0 functional was utilized to validate some important energies. Calculated total energies were integrated with \( k \)-point grids, resulting in \((5\times5\times1)\) and \((4\times4\times1)\) sampling for the Cu(111) and Cu(211) surfaces, respectively.

In the case of \( O_2 \), the formation energy of the modified Cu(111) surface is \(-0.3 \text{ eV} \) (see Fig.2). With increasing the concentration, the interstitial oxygen impurities stabilize the Cu(111) surface with a formation energy of \(-1.3 \text{ eV} \) (\( O_{10} \)). As the oxygen content is further increased to \( O_{40} \), the modified Cu(111) surface shows an enhanced roughness (see Fig.2) in comparison with the pristine Cu(111) surface. In contrast to the Cu(111) surface, the interstitial oxygen impurities are not stable at the Cu(211) subsurface. Although the calculated formation energies of Cu(211) surfaces suggest the Cu(211) surface can be stabilized by incorporated oxygen impurities, the critical point is that the oxygen impurities prefer to be adsorbed on the top of Cu(211) surface, instead of being present at the subsurface (see Fig.2). However, the adsorbed oxygen on the top of Cu(211) surface is definitely repulsive to a \( CO_2 \) molecule. Therefore, the catalytic activity of \( CO_2 \) reduction towards hydrocarbon on the Cu(211) surfaces of modified Cu electrodes should be much lower than that on the unmodified polycrystalline Cu electrodes. This is indeed consistent with the observations in the experiments of Li et al. Therefore, we conclude that the observed enhanced \( CO_2 \) reduction is not due to the contribution from Cu(211) and Cu(211) surfaces.

### Fig. 1
Side views of (a) Cu(111) and (b) Cu(211) surfaces with interstitial oxygen impurities. Cu and O atoms are represented in blue and red balls, respectively. Three cases of interstitial oxygen are denoted with \( t \), \( b \), and \( o \) at the Cu(111) subsurface; \( a \), \( b \), and \( c \) at the Cu(211) subsurface.

### Fig. 2
Calculated formation energies of (a) Cu(111) and (c) Cu(211) surfaces with a variety of studied concentration of interstitial oxygen impurities at subsurfaces, where the \( \Delta \mu \) was referred to a half energy of a \( O_2 \) molecule. The black dashed line is the reference (pristine Cu(111) and Cu(211) surfaces). The most stable (b) Cu(111) and (d) Cu(211) surfaces are shown, where Cu and O atoms are represented in blue and red, respectively.

Calculated d-band states of a pristine Cu(111) surface are shown in Fig.3, which is comparable with the previous calculated results. However, we have found the modified Cu(111) surface has more d-band states in the range from the Fermi level to \(-2 \text{ eV}\) below. In light of the d-band model, a \( CO_2 \) molecule should be bound with the modified Cu(111) surface much stronger, compared with a pristine Cu(111) surface. This results from a stronger repulsion between d-band states and antibonding states of \( C^* \) and \( O^* \) species (hereafter, we will use an asterisk to describe a adsorbed species on a surface, unless otherwise stated). In the case of \( O_{10} \) impurities, the calculated binding energy of \( CO_2 \) on the Cu(111) surface (\(-0.41 \text{ eV}\)) is much stronger, by \(-0.5 \text{ eV}\) compared with that on a pristine Cu(111) surface. Therefore, we understand that the enhanced activity of \( CO_2 \) electroreduction in the experiments of Li et al. was probably
due to a stronger binding strength of CO$_2$ molecules on the modified Cu electrodes. The active sites of the modified Cu electrodes are contributed from the modified Cu$_{0}(111)$ surface instead of modified Cu$_{0}(211)$ surface. As it is well-known, Cu(111) surfaces are the most stable facets on polycrystalline Cu electrodes. Hence, the improved activity on the Cu(111) surface can reasonably explain the observed high efficiency in the experiment.$^4$

Moreover, the HER on the unmodified Cu electrodes is dominant at a low overpotential.$^3$ However, the activity of the HER seems to be suppressed on the modified Cu electrodes.$^4$ The HER performance on different catalysts can be described in terms of a volcano curve, where the activity of catalysts is a function of the hydrogen binding strength on the surface of catalysts. The activity of the HER on the Pt(111) surface was demonstrated to be close to the optimal activity (the peak of volcano). In the present work, the computed hydrogen binding energy on a Pt(111) surface (-0.08 eV) is in agreement with the reported value.$^5$ On the pristine Cu(111) surface, the binding strength of hydrogen is slightly weaker (0.10 eV). However, the binding strength of hydrogen on the modified Cu$_{0}(111)$ surface is too strong, that is, -0.93 eV. The trend is also consistent with calculations using hybrid PBE0 functional (-1.51 eV). This argument can also help to understand why the CO$_2$ reduction can outcompete the HER at a low overpotential in the experiment.$^4$ In other words, the HER activity is strongly suppressed by the process of H$_2$ desorption on the modified Cu electrodes.

The next important issue is to understand why the CO and HCOOH evolution can take place at a quite low overpotential (-0.5 V vs. RHE). In the work of Hansen et al.$^{16}$ they had proposed two important factors for CO$_2$ reduction to obtain a high activity of CO evolution. In the case of the Au(211) surface, the *COOH species are not stable. The enhanced overpotential is helpful for CO evolution by means of stabilizing the *COOH species on the surface. In contrast to the Au(211) surface, *COH desorption becomes quite difficult from a Pt(211) surface due to the very strong binding energy of *CO species. Hence, they pointed out the two binding energies of *COOH and *CO are essentially responsible for the required overpotential in experiment. They proposed that for the CO evolution reaction the optimal catalysts should be able to stabilize *COOH species and possess facile desorption of resulting *CO species.

Our calculated $\Delta G$ of CO$_2$ reduction reactions are indeed in agreement with the proposed criteria. Our calculated binding energy indicates that the *COOH on the Cu$_{0}(111)$ surface is sufficiently stable (see Fig.4). The stability of *COOH can be explained in terms of the scaling relation on heterogeneous surfaces.$^{17,18}$ In other words, the stability of the *COOH is directly correlated with the binding strength of CO$_2$ molecule on the Cu$_{0}(111)$ surface. Moreover, the Cu$_{0}(111)$ surface has facile *CO desorption (0.01 eV) in the presence of adsorbed *OH species, in comparison with that of the Pt(211) surface.

From the energetic point of view, the HCOOH evolution reaction should be always more favorable in comparison with the CO evolution one (see Fig.4). However, the desorption of *HCOOH is more difficult than that of *CO, therefore, it was observed in the experiments that CO evolution outcompetes HCOOH evolution on the modified Cu electrodes at a low overpotential (<0.3 V). In addition, it was also observed that at higher overpotential (>0.3 V) the CO evolution fails in the competition. This is because the *HCOOH formation becomes exergonic at higher overpotentials. The required overpotential is ~0.28 V in our DFT calculations (PBE0: ~0.32 V), which is consistent with the minimal experimental overpotential of decreasing the amount of CO evolution (~0.3 V).$^4$

In principle, it is possible to manipulate the HCOOH and CO evolution by means of tuning the relative stability of some important species, namely, *CO, *COOH, and *HCOOH, as well as the desorption energies of *CO and *HCOOH. At the first step, we simply neglect the structural effects of modified catalysts and uniquely optimize the electronic structures. In light of the d-band model and the fact of weak reactivity on a pristine Cu(111) surface, we hope that the d-band states of the new catalyst are close to those of the Cu$_{0}(111)$ surface to

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**Fig.3** Calculated d-band states of a pristine Cu(111), the modified Cu$_{0}(111)$ and Cu$_{0}(111)$ in the O$_{h0}$ and C$_{b0}$ cases, respectively. The Fermi energies are specified to be zero.

**Fig.4** Calculated free energy diagrams of CO$_2$ electrochemical reductions to CO and HCOOH on (a) Cu$_{0}(111)$ surface at an overpotential of -0.5 V vs. RHE, and (b) Cu$_{0}(111)$ surface at an overpotential of -0.3 V vs. RHE.
improve the CO$_2$ binding strength (see Fig. 3). Meanwhile, the new catalyst must be stable under specific conditions. We screen a variety of elements close to oxygen in the Periodic Table, that is, C, N, and F elements, using the same atomistic models (see Fig. 1). We also use the same nomenclature in the following discussions. First, calculated formation energies implicate that Cu$_2$(111) surfaces are not stable. Additionally, in the Fe$_{120}$ case of modified Cu$_2$(111) surfaces, the interstitial F atoms prefer to aggregate in forming a F$_2$ molecule at the subsurface. Obviously, the F$_2$ molecule is likely to destroy the surface due to its volume expansion. In addition, we do not want to give rise to potential secondary pollution from our catalysts. Thus, nitrides and fluorides are not good precursors in experiments. Fortunately, we found the Cu$_2$(111) surfaces are stable with -1.21, -1.27, and -1.14 eV/C in the cases of CO$_2$, C$_n$O, and C$_n$, respectively. Meanwhile, the Cu$_2$(111) surfaces exhibit enhanced reactivity of CO$_2$ adsorption, compared with a pristine Cu(111) surface, because the effective d-band center of the Cu$_2$(111) surface shifts towards the Fermi level (see Fig. 4).

Furthermore, we have performed calculations based on the most stable Cu$_2$(111) surface in the case of Cu$_{120}$ impurities. Calculated free energy diagrams indicate that the pathway of HCOOH evolution is energetically more favorable than the CO evolution (see Fig. 4). Moreover, CO desorption from the Cu$_2$(111) surface is not preferred due to an adsorption energy of -0.7 eV (PBE0: -0.65 eV), which is significantly higher than that of the Cu$_2$(111) surface. In contrast, the HCOOH adsorption energy from the Cu$_2$(111) surface is only -0.2 eV (PBE0: -0.14 eV). Hence, the HCOOH evolution can always overcompete the CO evolution from the desorption point of view. Moreover, the *HCOOH formation is not very difficult compared with the formation of *COOH (PBE: -0.13 eV, PBE0: -0.11 eV). In addition, we found a stable intermediate, namely, *OCHO, on the Cu$_2$(111) surface. This intermediate can make use of another pathway to drive CO$_2$ reduction to the HCOOH evolution (see Fig. 4), and meanwhile suppress the CO evolution. Hence, one can expect that the efficiency of HCOOH evolution should be much higher than CO evolution.

The validations of our theoretical predictions need further experimental efforts.

In summary, we have performed Density Functional Theory calculations to elucidate the CO$_2$ reduction reactions at a low overpotential on the modified Cu electrodes in experiments. We have found the interstitial oxygen impurities can be stable at Cu(111) subsurface, which are able to improve the binding ability of CO$_2$ molecules on the modified Cu electrodes. Therefore, CO$_2$ reduction reactions become feasible at a low overpotential. The catalytic selectivity can be attributable to the competitions and compromise between CO desorption and *HCOOH formation. Our calculations are consistent with the observed transition from CO evolution to HCOOH evolution. Based on the better understanding concerning the previous experimental results, we performed further studies to propose a novel catalyst, that is, the carbon modified Cu electrodes. It has a better HCOOH selectivity in CO$_2$ electroreduction.

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References


Tune the electrochemical activity and selectivity of Cu electrodes by carbon and oxygen impurities at their subsurface.