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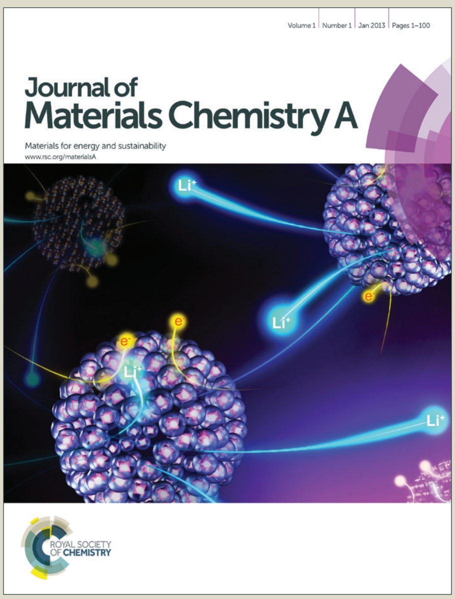

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ARTICLE TYPE

CO_2 Reduction at Low Overpotential on Cu Electrodes in the Presence of Impurities at Subsurface

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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_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_2 electroreduction, which has a better catalytic selectivity.

Carbon dioxide (CO_2) emission causes global climate change from an environmental point of view. CO_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_2 reduction can serve as fuels. In order to achieve benefits from CO_2 reduction, we need an efficient catalyst to reduce CO_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_2, simutaneously solving the storage issues of intermittent energies, *e.g.*, solar, wind, geothermal, etc.[1] Polycrystalline copper (Cu) electrodes have drawn a lot of attentions because they can be used to reduce CO_2 to hydrocarbon species.[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.[3]

Recently, Li *et al*[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_2O layers. With the modified Cu electrodes they can achieve a much better performance in CO_2 reduction to CO and HCOOH with a low overpotential of less than 0.5 V.[3] Catalytic selectivity is yet another important issue. In the above experiments of Li *et al.*,[4] the CO evolution reaction was preferred over the HCOOH evoluion 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_2 can be electrochemically reduced to a hydrocarbon at a high overpotential of ~1 V.[5] However, the activity and selectivity of CO_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_2 reduction at the active sites of modified Cu electrodes to elucidate the underlying chemical mechanism in the experiment.[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 acitve sites for chemical reations.[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 $Cu_O(111)$ and $Cu_O(211)$, respectively. In the $Cu_O(111)$ case, the initial sites of oxygen impurities are described using subscripts *t* (tetrahedral), *o* (octahedral), and *b* (below). For the $Cu_O(211)$ 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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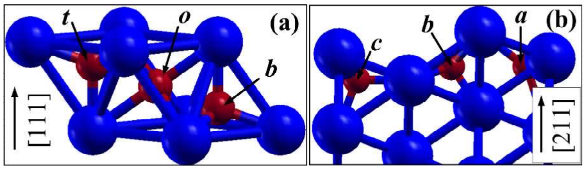

Fig.1 Side views of (a) Cu(111) and (b) Cu(211) surfaces with interstitial oxygen impurities. Cu and O atoms are represented in blue and red balls, respectively. Three cases of interstitial oxygen are denoted with *t*, *b*, and *o* at the Cu(111) subsurface; *a*, *b*, and *c* at the Cu(211) subsurface.

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

$$E_f = E_{tot} - E_{Cu} - n\mu_O ,$$

where E_{tot}, E_{Cu}, n, and μ_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 μ_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:[5]

$$H^+(aq) + e^- \leftrightarrow \frac{1}{2}H_2(g) ,$$

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, $\mu(H^+)+\mu(e^-)$, is equal to $\frac{1}{2}\mu(H_2)$ without applied external potential ($U = 0$ V). The free energy change, ΔG, 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.[7] Gaussian-type basis sets were used for H,[8] C,[9] O,[10] and Cu[11]. The difference of Cu(111) surface energies is ~0.03 eV/Å^2 compared with another basis set.[12] 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 (5×5×1) and (4×4×1) sampling for the $Cu_O(111)$ and $Cu_O(211)$ surfaces, respectively.

In the case of O_O, the formation energy of the modified $Cu_O(111)$ surface is -0.3 eV (see **Fig.2**). With increasing the concentration, the interstitial oxygen impurities stabilizes the $Cu_O(111)$ surface with a formation energy of -1.3 eV (O_{bt}). As the oxygen content is further increased to O_{bto}, the modified $Cu_O(111)$ surface shows an enhanced roughness (see **Fig.2**) in comparison with the pristine Cu(111) surface. In contrast to the $Cu_O(111)$ surface, the interstitial oxygen impurities are not stable at the $Cu_O(211)$ subsurface. Although the calculated formation energies of $Cu_O(211)$ 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 $Cu_O(211)$ surface is definitely repulsive to a CO_2 molecule. Therefore, the catalytic activity of CO_2 reduction towards hydrocarbon on the $Cu_O(211)$ surfaces of modified Cu electrodes should be much lower than that on the unmodified polycrystalline Cu electrodes.[3] This is indeed consistent with the observations in the experiments of Li *et al.*[4] Therefore, we conclude that the observed enhanced CO_2 reduction is not due to the contribution from Cu(211) and $Cu_O(211)$ surfaces.

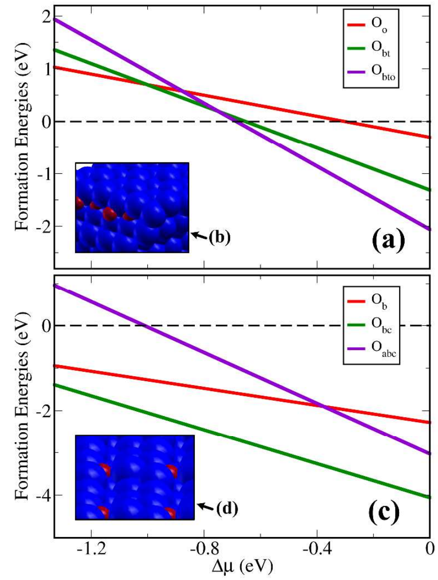

Fig. 2 Calculated formation energies of (a) $Cu_O(111)$ and (c) $Cu_O(211)$ surfaces with a variety of studied concentration of interstitial oxygen impurities at subsurfaces, where the $\Delta\mu$ was referred to a half energy of a O_2 molecule. The black dashed line is the reference (pristine Cu(111) and Cu(211) surfaces). The most stable (b) $Cu_O(111)$ and (d) $Cu_O(211)$ 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.[13] However, we have found the modified $Cu_O(111)$ surface has more d-band states in the range from the Fermi level to -2 eV below. In light of the d-band model,[14] a CO_2 molecule should be bound with the modified $Cu_O(111)$ surface more 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_{bto} impurities, the calculated binding energy of CO_2 on the $Cu_O(111)$ surface (-0.41 eV) is much stronger, by ~0.5 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.*[4] was propably 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 $Cu_O(111)$ surface instead of modified $Cu_O(211)$ 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]

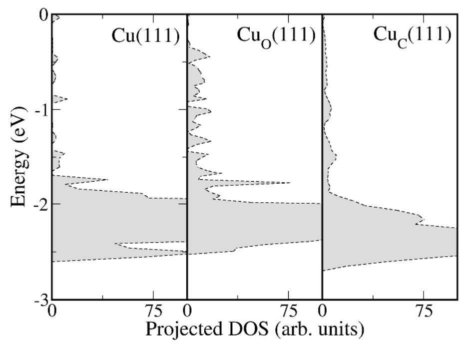

Fig.3 Calculated d-band states of a pristine Cu(111), the modified $Cu_O(111)$ and $Cu_C(111)$ in the O_{bto} and C_{bto} cases, respectively. The Fermi energies are specified to be zero.

Moreover, the HER on the unmodified Cu electrodes is dominant at a low overpotential.[5] 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 valcano 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 valcano). In the present work, the computed hydrogen binding energy on a Pt(111) surface (-0.08 eV) is in agreement with the reported value.[15] On the pristine Cu(111) surface, the binding strength of hydrogen is slightly weaker (0.10 eV). However, the binding strengh of hydrogen on the modified $Cu_O(111)$ 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, *CO 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 ΔG of CO_2 reduction reactions are indeed in agreement with the proposed criteria. Our calculated binding energy indicates that the *COOH on the $Cu_O(111)$ 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 $Cu_O(111)$ surface. Moreover, the $Cu_O(111)$ surface has facile *CO desorption (0.01 eV) in the presence of adsorbed *OH species, in comparison with that of the Pt(211) surface.

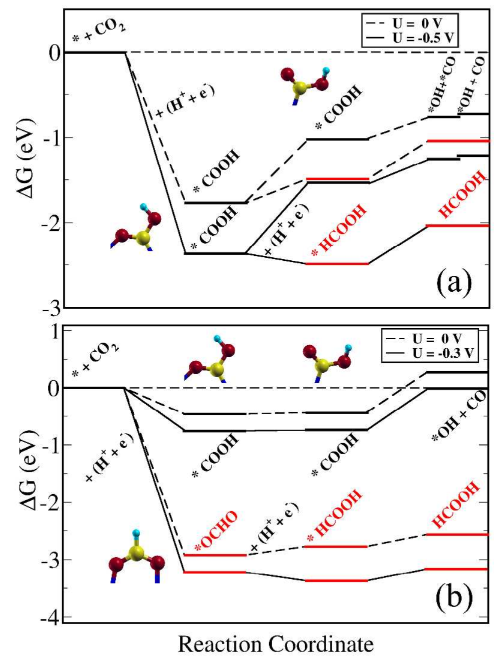

Fig.4 Calculated free energy diagrams of CO_2 electrochemical reductions to CO and HCOOH on (a) $Cu_O(111)$ surface at an overpotential of -0.5 V vs. RHE, and (b) $Cu_C(111)$ surface at an overpotential of -0.3 V vs. RHE.

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 $Cu_O(111)$ surface to 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 $Cu_N(111)$ surfaces are not stable. Additionally, in the F_{bto} case of modified $Cu_F(111)$ 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 $Cu_C(111)$ surfaces are stable with -1.21, -1.27, and -1.14 eV/C in the cases of C_O, C_{to} and C_{bto}, respectively. Meanwhile, the $Cu_C(111)$ surfaces exhibit enhanced reactivity of CO_2 adsorption, compared with a pristine Cu(111) surface, because the effective d-band center of the $Cu_C(111)$ surface shifts towards the Fermi level (see **Fig. 4**).

Furthermore, we have performed calculations based on the most stable $Cu_C(111)$ surface in the case of C_{bto} 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 $Cu_C(111)$ 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 $Cu_O(111)$ surface. In contrast, the HCOOH desorption energy from the $Cu_C(111)$ surface is only ~0.2 eV (PBE0: ~0.14 eV). Hence, the HCOOH evolution can always outcompete 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 $Cu_C(111)$ 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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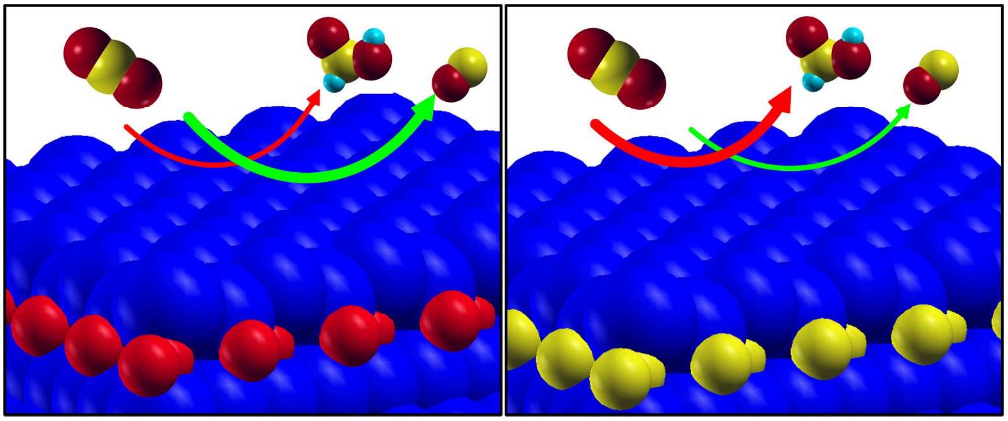

Tune the electrochemical activity and selectivity of Cu electrodes by carbon and oxygen impurities at their subsurface.
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