Cu metal embedded in oxidized matrix catalyst to promote CO₂ activation and CO dimerization for electrochemical reduction of CO₂

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We propose and validate with quantum mechanics methods a unique catalyst for electrochemical reduction of CO₂ (CO₂RR) in which selectivity and activity of CO and C₂ products are both enhanced at the borders of oxidized and metallic surface regions. This Cu metal embedded in oxidized matrix (MEOM) catalyst is consistent with observations that Cu₂O-based electrodes improve performance. However, we show that a fully oxidized matrix (FOM) model would not explain the experimentally observed performance, and we show that the FOM is not stable under RR conditions. This electrostatic tension between the Cu⁺ and Cu²⁺ surface sites responsible for the MEOM mechanism suggests a unique strategy for designing more efficient and selective electrocatalysts for CO₂RR to valuable chemicals (HCO₃⁻), a critical need for practical environmental and energy applications.

Electrochemical reduction of CO₂ (CO₂RR) to valuable chemicals is an essential strategy to achieve industrial-scale reduction of the carbon footprint under mild conditions and to provide a means of storing electrical power from intermittent renewable sources into stable chemical forms (1). Cu is the prototype electrocatalyst for CO₂RR, because it is the only pure metal that delivers appreciable amounts of methane and ethylene plus minor alcohol products (2–7), but it suffers from high overpotentials and very significant hydrogen evolution reactions (HERs). Consequently, tremendous efforts are being made to develop more efficient and selective electrocatalysts, for example by surface modification (8) and by nanoparticle (9, 10) and nanowire (11) engineering.

We examine here the mechanism by which Cu₂O-based electrodes are observed to improve both efficiency and selectivity for C₂ products (12–15), which also suppresses HERs by several-fold. Because Cu₂O is subject to reduction (back to Cu metal) under CO₂RR conditions, the improved performance was initially attributed to Cu metal surface morphology (8, 16). But a more recent experiment (15) showed that Cu⁺ sites can survive on the Cu surface for the course of CO₂RR. Importantly, a Cu sample that is first oxidized and then reduced using an H₂ plasma leads to performance substantially worse than that of the oxidized sample, despite both having similarly roughened surfaces.

This provides solid evidence that surface Cu⁺ plays an essential role in promoting the efficiency and selectivity of CO₂RR. However, experiments have provided no clue about how surface Cu⁺ affects the mechanisms of CO₂RR. Moreover, no previous theoretical efforts have elucidated its role.

To understand the promising results achieved with Cu₂O-based electrodes, we investigated three distinct models aimed at unraveling the role of surface Cu⁺ in shaping the free energy profiles of two key steps for CO₂RR. Here we carry out quantum mechanics (QM) calculations at constant potential by using our grand canonical methodology (17, 18) that uses the charge-asymmetric nonlocally determined local-electric (CANDLE) implicit solvation model (19) to achieve constant electrochemical potential (not constant number of electrons) within the framework of joint density functional theory (JDFT) (20, 21) (details in Computational Details). The three key steps we focus on are (i) CO₂ activation, which we previously showed to be the rate-determining step (RDS) for CO production on pure Cu (22); (ii) CO dimerization, which we previously showed to be the RDS for forming C₂ products from CO on pure Cu (17, 18); and (iii) C₁ product formation, which we find to compete with C₂ products for pure Cu.

We find that the surface Cu⁺ by itself actually deteriorates the performance of CO₂RR. Instead we show that it is synergy between surface Cu⁺ and surface Cu²⁺ that improves significantly the kinetics and thermodynamics of both CO₂ activation and CO dimerization, while making C₁ unfavorable, thereby boosting the efficiency and selectivity of CO₂RR. These results provide a unique concept for designing improved electrocatalysts. To illustrate this synergy we consider the case with an applied potential U = −0.9 V (referenced to standard hydrogen electrode (SHE)), which is where CO production reaches the peak and C₂ production begins on the oxide electrode (15). The free energies at any other U can be calculated using Table S1.

Fig. 1 shows the three surface models we used to probe the role of surface Cu⁺ in CO₂RR. Fig. 1A shows the metallic matrix (MM), where the pristine Cu₁₁₁ surface serves as a reference model for pure MM that has only Cu⁰ on the surface Fig. 1B shows the fully oxidized matrix (FOM), where the stoichiometric nonpolar Cu₂O₁₁₁ surface serves as a model for a FOM with only Cu⁺ on the surface. Here we find two types of Cu⁺ surface

Significance

A most promising approach to boosting both efficiency and selectivity for electrochemical reduction of CO₂ (CO₂RR) is using Cu₂O-based electrodes, and the surface Cu⁺ is believed to play an essential role that is totally unclear from both experiment and theory. We find that the surface Cu⁺ by itself actually deteriorates the performance of CO₂RR. Instead we propose a Cu metal embedded in oxidized matrix (MEOM) model and show that it is synergy between surface Cu⁺ and surface Cu²⁺ present in the MEOM model that improves significantly the kinetics and thermodynamics of both CO₂ activation and CO dimerization, thereby boosting the efficiency and selectivity of CO₂RR. The MEOM model serves as a unique platform for design of better electrocatalysts for CO₂RR.

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sites: \((\text{Cu}^+)_{\text{CUS}}\), a coordinatively saturated \(\text{Cu}^+\) site that is bonded to two O atoms, and \((\text{Cu}^+)_{\text{CUS}}\), a coordinatively unsaturated site that is bonded to only the one O atom directly below it (examples are marked in Fig. 1B). The \((\text{Cu}^+)_{\text{CUS}}\) is believed to be the active site (ref. 23 and references therein). However, it has been suggested by both theory (24) and experiment (25) that such \((\text{Cu}^+)_{\text{CUS}}\) sites are likely missing under oxygen-rich conditions (e.g., oxygen plasma treatment). More recent theoretical work (26) has shown that \((\text{Cu}^+)_{\text{CUS}}\) sites are favored under CO\text{2}\text{RR} conditions at neutral pH. Here we focus on the role of active surface \(\text{Cu}^+\) in shaping the energetics and mechanisms of CO\text{2}\text{RR}, rather than stability. Fig. 1C shows metal embedded in oxidized matrix (MEOM), a partially reduced \(\text{Cu}_2\text{O}(111)\) surface in which one-quarter of the surface is reduced. This serves as a conceptual model for our MEOM in which both \(\text{Cu}^0\) and \(\text{Cu}^+\) are present on the surface. We find that this leads to active \((\text{Cu}^+)_{\text{CUS}}\) sites at the edge of metallic \(\text{Cu}^0\) regions that play an essential role in the enhanced activity. Our MEOM catalyst site mimics the case for CO\text{2}\text{RR} operation, where the majority of surface stays oxidized but some reduced regions are created.

We focus here on the (111) surface orientation, because it is the most stable among \(\text{Cu}_2\text{O}\) surfaces (27) and has the fastest kinetics for Cu surface oxidation (28) (thus the most likely oxide surface orientation from oxidation of Cu foil). In the experiment that directly compared the metal with oxide surfaces (15), the measured onset potentials for \(\text{C}_2\text{H}_4\) production on Cu metal surfaces are \(-1.2\) V to \(-1.1\) V (this is the value for both electropolished and roughened surfaces obtained by first oxidizing and then reducing the Cu foil with hydrogen plasma), which are the same as the onset potentials measured on a Cu(111) single crystal electrode (\(-1.2\) V to \(-1.1\) V), but very different from the value of \(-0.8\) V to \(-0.6\) V measured on Cu(100) (29, 30).

**CO\text{2} Activation**

**MM Model.** We find that physisorption of CO\text{2} (CO\text{2,phys}) on the MM model leads to a noncovalent bond distance of 3.84 Å between the C atom of linear CO\text{2} and the Cu surface (C-Cu; Fig. S1A), which is similar to our previous study (22). Forming chemisorbed CO\text{2} (CO\text{2,chem}) from this CO\text{2,phys} involves a transition state (TS) that bends CO\text{2} with C-Cu\text{S} = 2.36 Å, and the resulting CO\text{2,chem} is asymmetrically adsorbed, with a surface CuO = 2.04 Å, whereas the second O atom pointing away from the surface to form a hydrogen bond (1.52 Å) to a surface H\text{2}\text{O} bonded to a nearby Cu\text{0} (Fig. S1C and Fig. 2). On the MM model the activation free energy barrier is \(\Delta G^\ddagger = 0.49\) eV at 298 K, similar to the value (0.43 eV) for Cu(100) in our previous study (22).

**FOM Model.** It was proposed (23) that in the FOM model CO\text{2} can adsorb at the (Cu\text{+})\text{CUS} site with a 2.09-Å bond of one O to (Cu\text{+})\text{CUS}. However, exposed to the electrolyte, the (Cu\text{+})\text{CUS} sites are mostly occupied by H\text{2}\text{O} molecules [strong electronic binding energy of \(\Delta E = -0.98\) eV, much larger than that for CO\text{2} (\(\Delta E = -0.31\) eV)]. Thus, the initial structure for CO\text{2} activation on the FOM model is still physisorption of CO\text{2} with a 4.07-Å distance between the C atom of linear CO\text{2} and O\text{, the closest surface O atom (Fig. S2A). We find a \(\Delta G^\ddagger = 0.56\) eV to convert this CO\text{2,phys} to a surface carbonate (Fig. 2), which can subsequently be released into the electrolyte, thereby reducing
the FOM surface. Therefore, CO₂ activation in the FOM model has a barrier 0.07 eV higher than the MM model and involves a different mechanism that does not lead to the key intermediate (chemisorbed CO₂) for CO production. This indicates that the experimentally observed promotion of CO production using oxidized electrodes (12, 13, 15) cannot be explained with the presence only of surface Cu⁺.

**MEOM Catalyst.** In contrast, the MEOM surface has a metallic Cu⁰ region bordered by the Cu⁺ oxide matrix. Here physisorbed CO₂ is favored on top of the Cu⁺ region (Fig. S3A), and the activation of CO₂ proceeds through a TS that bends CO₂ just as in the MM case (Fig. S3B), leading to the asymmetrically chemisorbed CO₂ on the Cu⁰ region. But now the free energy barrier is ∆Ĝ = 0.27 eV, which is 0.22 eV lower than for the MM model. Moreover, the chemisorbed CO₂ is ∆G = −0.26 eV more stable than physisorbed CO₂ on the MEOM catalyst (Fig. 2).

This drastic improvement in both kinetics and thermodynamics for the MEOM catalyst is due to the presence of (Cu⁺)Cu⁺ sites that bind H₂O molecules at the edge of the Cu⁰ region. This H₂O molecule on the (Cu⁺)Cu⁺ site forms strong hydrogen bonds to the CO₂, stabilizing both the TS and the final state (FS) (Fig. 2). This opens a channel in which the negative charge accumulated on the O atom of the CO₂ during activation is distributed to the Cu⁺ region, thus stabilizing both the TS and the FS.

Summarizing, only this MEOM catalyst with both surface Cu⁺ regions (bonds to activated CO₂ and Cu⁺) and neighboring CO@Cu⁺ (binds to activated CO₂) has the ability to enable promotion of CO₂ activation, with favorable kinetics and thermodynamics. This explains the experimental observation that both the onset potential and the peak Faradaic efficiency for CO production are improved for CO₂RR on oxide-based electrodes (12, 13, 15). We propose that our MEOM catalyst might also provide the mechanism by which partially oxidized atomic cobalt layers improve formate production (31).

**CO Dimerization**

**MM Model.** CO dimerization on the MM model has been thoroughly studied by us and others (17, 32). The initial structure of two well-separated adsorbed CO molecules (Fig. S4A) goes through a TS that tilts and draws the two COs close (Fig. S4B), with ∆Ĝ = 1.10 eV, to form an OCCO surface species with a 1.52-Å C-C bond (Fig. S4C).

**FOM Model.** In contrast, CO dimerization in the FOM model takes a distinctly different path. A CO molecule introduced near the FOM surface (either direct or from CO₂RR) binds to the (Cu⁺)Cu⁺ site by ∆E = −1.62 eV, displacing the H₂O (∆E = −0.98 eV). Thus, CO dimerization starts with two strongly adsorbed CO molecules on neighboring (Cu⁺)Cu⁺ sites (Fig. S5A), which proceeds through an asymmetric TS (Fig. S5B) that rotates both CO molecules to have O atoms bonded to the (Cu⁺)Cu⁺ sites (initially C atoms were bonded) with the C atom of one CO molecule bonded to the (Cu⁺)Cu⁺ site in between. The resulting OCCO surface species (Fig. S5C and Fig. 3) is formed with a C=C double bond (1.30 Å) with each C atom bonded to the middle (Cu⁺)Cu⁺. This is the only stable CO dimer on the FOM surface, but the formation barrier is ∆Ĝ = 3.15 eV, and the product has a free energy unstable by ∆G = 2.25 eV. Thus, the presence of only Cu⁺ at the active surface cannot explain the experimental observation that C₂ products are promoted with oxidation-treated electrodes (13–15).

**MEOM Catalyst.** On the MEOM surface, CO also adsorbs on the (Cu⁺)Cu⁺ site (CO@Cu⁺), more stable by 0.48 eV than on the metallic Cu⁰ region (CO@Cu⁰). With MEOM, CO dimerization from two neighboring CO@Cu⁺ is the same in nature as that on the FOM surface, so it would lead to the same ∆Ĝ = 3.15 eV) as for the FOM. However, CO dimerization starting with CO@Cu⁰ and a neighboring CO@Cu⁺ (Fig. S6A) has a modest barrier of ∆Ĝ = 0.71 eV to form the OCCO surface species, in which the two C atoms are still bonded to the Cu⁺ and Cu⁰ regions (Fig. S6C), leading to ∆G = 0.12 eV (Fig. 3). The favorable energetics of this C-C coupling can be understood by noting that the C atom of CO@Cu⁺ is positively charged (Mulliken charge of +0.11) whereas the C atom of CO@Cu⁰ is negatively charged (Mulliken charge of −0.31) due to back donation. Thus, the attractive electrostatics between the two Cs assists C-C bond formation. It is this favorable dimerization process on the MEOM model that improves both kinetics and thermodynamics of the RDS for C₂ products, compared with the traditional MM model (Fig. 3). Thus, we propose that promotion of C₂ products for oxidation-treated electrodes arises from the MEOM surface via the mechanism described above (13–15).

The major C₂ products from CO₂RR have been reported to be either ethylene (13, 15) or ethanol (14), where the major difference in these experiments is the pH (neutral pH for ethylene and basic pH for ethanol). We have shown recently (18) that the energetics of surface water determine the selectivity of alcohol vs. hydrocarbon products. We found that at neutral pH it is favorable for surface water to donate a proton for dehydroxylation to form hydrocarbon products. Whereas in basic pH the ability of surface water to dehydroxylate the surface species is suppressed (because the product OH⁻ is less favorable), favoring instead the alcohol product (ethanol).

**C₃ Pathways**

Next we consider the possible pathways for forming C₃ with the MEOM surface. Here we expect CO@Cu⁺ and H@Cu⁰. Interestingly, the COH pathway previously proposed by us (17, 33) is an unreasonable option, because COH@Cu⁺ is higher than CHO@Cu⁺ by ∆G = 1.86 eV. This also eliminates the COCOH pathway for C₂ products we previously proposed (17). On the other hand, the CHO pathway has a reasonable free energy barrier of ∆Ĝ = 1.13 eV (Fig. 3) at neutral pH, which is still significantly higher than the ∆Ĝ = 0.71 eV for C-C coupling with CO@Cu⁺ and CO@Cu⁰. Consequently the stability of CO@Cu⁺ (which is more resistant to hydrogenation) blocks the C₃ products. This selectivity for C₂ over C₃ is intrinsic and not due to the external local high-pH effect as speculated previously (13, 15).

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Notes on the MEOM Catalyst

The MEOM concept is in fact a synergistic metal and oxidized matrix cocatalyst, with both ingredients directly participating in catalysis. Thus, for the MEOM model to be effective, it is necessary for the metal surface to be level with the oxidized matrix surface so that the surface species can interact via proper geometries. Therefore, a suitable scheme to generate the MEOM catalyst is deriving the metal directly from the oxidized matrix surface as in our construction of the MEOM model, which is also consistent with the current experimental strategy. This scheme can be naturally extended to starting with a mixed oxidized matrix (e.g., CuO/Ag2S) for alternative oxidized matrices.

Summary

We present the MEOM model for a partially oxidized Cu surface and show that this model leads to plausible mechanisms to explain the experimental findings that CO2RR can be made more efficient and selective, using oxidized electrodes. However, MEOM requires that we only partially oxidize the surface. This MEOM model presents a unique guideline for design of improved CO2RR electrocatalysts. In contrast to previous speculations, we find that the active surface Cu+ sites alone do not improve the efficiencies of CO2RR and indeed deteriorate the efficiency. Instead the synergy between active surface Cu+ and Cu2+ regions present in the MEOM model is responsible for improving significantly the kinetics and thermodynamics of both CO2 activation and CO dimerization while impeding C1 pathways, the key steps for efficiency and selectivity of CO2RR.

Based on our MEOM model, we conclude that the oxidized matrix (CuO) is unstable under CO2RR working conditions. We find that the role of the Cu(O) is mainly electrostatic in diluting the negative charge built up on the CO2, as it then transits from physisorbed to chemisorbed structures, which in turn makes the C atom of CO positively charged. This MEOM model suggests alternative oxidized matrices (like Ag2S) could also deliver similar electrocatalytic contributions, leading to much improved electrochemical stabilities.

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Supporting Information

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Computational Details. The calculations were first performed with the VASP package (34–36), using the Perdew–Burke–Ernzerhof (PBE) flavor (37) of DFT and the projector augmented wave (PAW) method (38) to account for core-valence interactions. The kinetic energy cutoff for plane-wave expansions was set to 400 eV, and reciprocal space was sampled by a Γ-centered Monkhorst–Pack scheme with a grid of $3 \times 3 \times 1$. The $4 \times 4 \text{Cu}(111)$ and $2 \times 2 \text{Cu}_2\text{O}(111)$ surface slabs were constructed with three layers (bottom layer fixed), using the experimental lattice parameters of 3.615 Å and 4.2745 Å, respectively, with vacuum layers of at least 15 Å.

The convergence criteria are $1 \times 10^{-5}$ eV and $1 \times 10^{-7}$ eV energy differences for solving for the electronic wavefunction for local minima (initial states (ISs) and FSs) and TSs, respectively. The Methfessel–Paxton smearing of second order with a width of 0.1 eV was applied. All IS, TS, and FS geometries (atomic coordinates) are converged to within $3 \times 10^{-2}$ eV/Å for maximal components of forces. The TS search was conducted by using the climbing-image nudged elastic band (CI-NEB) method (39) to generate initial guess geometries, followed by the dimer method (40) to converge to the saddle points.

Zero-point energy (ZPE), enthalpy, and entropy contributions to free energies at room temperature (298.15 K) were calculated from vibrational modes of surface species, which were computed with the finite difference approach. Note that very low-frequency modes were obtained in some cases, because the explicit water molecules are not properly constrained by the hydrogen-bonding network present in water bulk. Such low-frequency modes can cause unphysically large entropy contributions, so they were reset to a threshold value of 60 cm$^{-1}$, corresponding to the acoustic translational mode of the six-member rings in water bulk (41, 42).

For the CO hydrogenation step where the surface H model was used to locate the TS, the IS was referenced back to the

$$H^+(H_3O^+/H_2O) + e^- \text{ pair through the free energy difference between the surface H and H}_2(g),$$

based on the half-cell reactions,

$$\text{H}_3\text{O}^+ + e^- = \frac{1}{2} \text{H}_2(g) + \text{H}_2\text{O} \quad \Delta G = 0.0592 \times \text{pH (eV)},$$

$$\text{H}_2\text{O} + e^- = \frac{1}{2} \text{H}_2(g) + \text{OH}^- \quad \Delta G = 0.0592 \times \text{pH (eV)}.$$ 

Thus, the pH effect is introduced into the free energy profile with the reference. In addition to vibrational contributions, the translational and rotational contributions to the free energy of H$_2$(g) were included, assuming the ideal gas model.

The explicit constant electrochemical potential ($\mu_e$) calculations with the implicit CANDLE solvation model (19) were performed upon all IS, TS, and FS geometries, using JDFTx (43). The Garrity–Bennett–Rabe–Vanderbilt (GBRV) (44) ultrasoft pseudopotentials (USPP) were used, with a plane-wave cutoff of 544 eV (20 a.u.). All other settings are similar to those in VASP calculations. The ionic screening of net charges resulting from the constant $\mu_e$ condition was achieved with cation (0.1 M K$^+$) and anion (0.1 M F$^-$) components in the fluid model (21) under the JDFT framework (20). The algorithm used by JDFTx variationally minimizes the grand free energy at fixed electron chemical potential with respect to Kohn–Sham orbitals (45), fluid bound charge, and an auxiliary Hamiltonian for the occupations (46). Previously we found that the relative free energies (barriers $\Delta G^\neq$ and reaction energies $\Delta G$) are linearly dependent on the applied potential $U$ for $|U| < \sim 2$ V [vs. standard hydrogen electrode (SHE)] (17), so the $U$ dependence of all $\Delta G^\neq$ and $\Delta G$ was calculated assuming a linear relationship between $U = 0.0$ V and $-1.2$ V. Note that here all Us are referenced to SHE.

Fig. S1. Top and side views of (A) IS, (B) TS, and (C) FS for the CO$_2$ activation on Cu MM. The marked distances are between the C atom of CO$_2$ and the Cu surface. In the FS (chemisorbed CO$_2$), Cu-C and Cu-O bond lengths are 2.05 Å and 2.04 Å, respectively.

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Fig. S2. Top and side views of (A) IS, (B) TS, and (C) FS for the CO$_2$ activation on FOM. The marked distances are between the C atom of CO$_2$ and the surface O atom that is bonded to CO$_2$ in the FS. Note that a surface carbonate is formed in the FS.

Fig. S3. Top and side views of (A) IS, (B) TS, and (C) FS for the CO$_2$ activation on MEOM. The marked distances are between the C atom of CO$_2$ and the Cu metallic region surface. In the FS (chemisorbed CO$_2$), Cu-C and Cu-O bond lengths are 2.02 Å and 2.04 Å, respectively.
Fig. S4. Top and side views of (A) IS, (B) TS, and (C) FS for the CO dimerization on Cu MM. The marked distances are between the two C atoms of CO.

Fig. S5. Top and side views of (A) IS, (B) TS, and (C) FS for the CO dimerization on FOM. The marked distances are between the two C atoms of CO. Note that the O atoms of CO are colored yellow for clarity.
Fig. S6. Top and side views of (A) IS, (B) TS, and (C) FS for the CO dimerization on MEOM. The marked distances are between the two C atoms of CO. Note that the O atoms of CO are colored yellow for clarity.

Fig. S7. Bader charges for representative sites on (A) FOM and (B) MEOM surfaces.

Table S1. Free energy barriers ($\Delta G^\ddagger$) and reaction free energies ($\Delta G$) for all key reactions

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$\Delta G^\ddagger$, eV</th>
<th>$\Delta G$, eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO$_2$(phys) = CO$_2$(chem) on M</td>
<td>0.5914 + 0.1117 × U</td>
<td>0.5021 + 0.3356 × U</td>
</tr>
<tr>
<td>CO$_2$(phys) = CO$_2$(chem) on FOM</td>
<td>0.6140 + 0.0593 × U</td>
<td>0.2508 + 0.1488 × U</td>
</tr>
<tr>
<td>CO$_2$(phys) = CO$_2$(chem) on MEOM</td>
<td>0.3636 + 0.1077 × U</td>
<td>0.0407 + 0.3392 × U</td>
</tr>
<tr>
<td>2CO = OCCO on M</td>
<td>1.1664 + 0.0764 × U</td>
<td>1.0812 + 0.2407 × U</td>
</tr>
<tr>
<td>2CO = OCCO on FOM</td>
<td>3.2747 + 0.1383 × U</td>
<td>2.8487 + 0.6696 × U</td>
</tr>
<tr>
<td>2CO = OCCO on MEOM</td>
<td>0.8602 + 0.1688 × U</td>
<td>0.4670 + 0.3828 × U</td>
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