Surfaces, Interfaces, and Catalysis; Physical Properties of Nanomaterials and Materials

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J. Phys. Chem. Lett., **Just Accepted Manuscript** • DOI: 10.1021/acs.jpcllett.8b00959 • Publication Date (Web): 22 May 2018

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Surface Ligand Promotion of Carbon Dioxide Reduction through Stabilizing Chemisorbed Reactive Intermediates

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ABSTRACT: We have explored functionalizing metal catalysts with surface ligands as an approach to facilitate electrochemical carbon dioxide reduction reaction (CO₂RR). To provide a molecular level understanding of the mechanism by which this enhancement occurs, we combine *in situ* spectroscopy analysis with an interpretation based on quantum mechanics (QM) calculations. We find that a surface ligand can play a critical role in stabilizing the chemisorbed CO₂, which facilitates CO₂ activation and leads to a 0.3 V decrease in the overpotential for carbon monoxide (CO) formation. Moreover, the presence of the surface ligand leads to nearly exclusive CO production. At -0.6 V (versus reversible hydrogen electrode, RHE), CO is the only significant product with a faradic efficiency of 93% and a current density of 1.9 mA cm⁻². This improvement corresponds to 53-fold enhancement in turnover frequency compared with the Ag nanoparticles (NPs) without surface ligands.

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3 Directly using CO₂ as carbon-based fuel feedstock is promising for developing a sustainable
4 carbon-based economy, which, could also reduce the impact of CO₂ on climate change.¹⁻⁹
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6 Electroreduction of CO₂ to CO is of particular importance due to the central role of CO in
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8 reducing CO₂ to hydrocarbon fuels. Although the redox potential of CO₂ to CO is only -0.11 V
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10 (vs. RHE, hereafter all potentials referenced to RHE), activation of CO₂ always requires
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12 significant overpotential due to its inertness.^{10,11} Until now the reported performance of CO₂
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14 catalysis remains far from meeting the minimum requirement for large-scale applications.
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16 Therefore, it would be useful to develop rational design principles for facilitating improved
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18 CO₂RR.
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24 Among transition metals, noble metal Au and Ag exhibit superior performance in reducing
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26 CO₂ to CO. Ag is more appealing, considering the lower cost compared with Au. Meanwhile, the
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28 excellent mechanical property of Ag (such as high ductility) allows further fabrication to
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30 improve the activity and stability. Ag is a promising catalyst for both laboratory applications and
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32 future industrial production. Extensive efforts have been devoted to improving CO₂RR
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34 performance for Ag-based electrodes, including tuning their defect site, size, shape, and
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36 component.¹²⁻²¹ Jiao et al. reported a nanoporous Ag achieved for 92% selectivity under a
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38 potential of -0.6 V.¹⁴ Luo and coworkers developed triangular Ag nanoplates with predominant
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40 Ag(100) facets to reach 96.8% selectivity under -0.86 V.²² As a more facile and efficient
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42 approach, surface ligands have been reported to promote CO₂RR. For example, amine-
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44 functionalized ligands, cysteamine (HS-CH₂-CH₂-NH₂), can significantly improve the CO₂RR
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46 with reduced onset potential and 84.4% selectivity for CO formation under -0.75 V. Hwang et al.
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48 proposed that this enhancement is due to Ag-S interaction inducing surface localization of the
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50 unpaired electron.¹³ However, for enzymes of hydrogenase or CO-dehydrogenase, the amino
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residues can also assist the H₂ or CO₂ absorption and activation by coordinating interactions with closed metal ions.^{23,24} Thus, in addition to the electron-dislocation effect reported previously, we suspected that the surface ligands could also stabilize chemisorbed CO₂ geometrically. Herein, we employed QM to investigate the CO₂RR on Ag with an attached cysteamine ligand to stabilize the process of physisorbed CO₂ to chemisorbed CO₂.

In our QM simulations, we employed a four-layer 3×3 Ag(111) surface, with one or two cysteamine molecules chemisorbed to the surface via Ag-S bonds, corresponding to a surface concentration of 1/9 ML to 2/9 ML. We placed 32 water molecules on the surface forming five layers of explicit water to simulate the electrolyte/electrode interface.

One CO₂ molecule was inserted, and after 20 ps of ab initio molecular dynamics (AIMD) simulations we found that the average distance between CO₂ (the center of mass) and Ag surface is 3.74 Å, which is a typical range of non-bonded interaction indicating a physisorbed state of CO₂ on Ag surface. Such physisorbed CO₂ on Ag is similar as that we observed on copper (Cu) electrode (3.67 Å).^{25,26} In our previous work, we found that the formation of chemisorbed CO₂ from physisorbed CO₂ is the rate-limiting step in CO₂RR to CO.²⁵ Thus, we applied a constraint force to drive the chemical reactions from physisorbed CO₂ to chemisorbed CO₂ by taking the distance (Z_{CO_2}) between CO₂ (the center of mass) and Ag surface as a collective variable (the simulation details are in the supporting information). The calculated free energy profiles are shown in Figure 1C. For the pure Ag case, the free energy is a minimum at $Z=3\text{Å}$, corresponding to a van der Waals or physisorbed state, indicating that chemisorbed CO₂ is not stable on the clean Ag surface. A likely pathway for CO₂ reduction on Ag would be electron-coupled proton transfer to form *COOH, but we expect there to be little chance to capture the chemisorbed CO₂ on Ag surface at the operation potential in CO₂RR. As the applied biasing force is changed

continuously, we find that physisorbed CO₂ starts to convert to chemisorbed CO₂ as the distance between CO₂ and the topmost Ag atoms approach 1.60 Å. Instead of a “mixed coordination” as we found on Cu (100),²⁵ the chemisorbed CO₂ on Ag is in the configuration of “carbon coordination” as shown in Figure 1B. The AIMD simulation shows that there is always one neighbor water molecule forming a hydrogen bond to stabilize the chemisorbed CO₂. At this distance, the free energy is 0.6 eV, indicating that the minimum applied a potential to activate CO₂ on Ag(111) is -0.6 V. Thus, this chemisorbed CO₂ remains very unstable, immediately returning to physical adsorbed CO₂ after removing the constraint.

Figure 1. (A) chemisorbed CO₂ on cysteamine functionalized Ag(111) surface. (B) Chemisorbed CO₂ on Ag(111) surface. (C) The free energy profile of the CO₂ approaching surface. Only the water molecules directly forming hydrogen bond are shown (the remaining 31 or 30 solvent water molecules are removed for clarity). The hydrogen bonds are shown as a slashed line. The colors are Ag in silver, C in gray, O in red, N in blue, S in yellow and H in white.

However, in the case of Ag-S-CH₂-CH₂-NH₂ chemisorbed CO₂ is much more stable, especially when the cysteamine forms a cis-configuration on the surface. In this case, the nitrogen (N) atom from cysteamine binds to the surface, preventing protonation of -NH₂ to form -NH₃⁺ which is the stable form in bulk solution at this pH condition. As the distance between CO₂ from the surface reaches 2.12 Å (at a distance 0.52 Å more extended than on pure Ag), we find chemisorbed CO₂ as shown in Figure 1A. AIMD simulation snapshot shows that both water and terminal NH₂ group provide hydrogen bond (HB) to chemisorbed CO₂ as shown in Figure 1A. The extra HB due to the cysteamine may further stabilize chemisorbed CO₂. As shown in figure 1C, the chemisorbed CO₂ is a local minimum in the free energy profile. Thus, it is possible that chemisorbed CO₂ is detectable experimentally as a metastable intermediate. With Ag-S-CH₂-CH₂-NH₂, the free energy for activating CO₂ decrease to 0.32 eV. Thus, we estimate that CO₂ activation on Ag-S-CH₂-CH₂-NH₂ would occur at a 0.28 V less negative onset potential than for pure Ag, consistent with 0.3 V decrease in experiment (as shown in Figure 4).

Previously, such stabilization effects had been rationalized as pure electronic effects arising from the Ag-S interaction.¹⁶ Instead, our AIMD atomic structure analysis reveals that geometric stabilization effect also plays an important role. To elucidate the influence of electron localization and geometry stabilization effect on CO₂RR, we carried out three types of experiments:

- ligand-free Ag NPs,
- cysteamine-capped Ag NP (C2-Ag),
- 11-Amino-1-undecanethiol capped Ag NP (C11-Ag).

Both C₂-Ag and C₁₁-Ag have a similar localization effect, but for C₁₁-Ag the carbon chain is too long to form a complex with chemisorbed CO₂ so that we find no geometry stabilization. All

the prepared Ag NPs have a similar core diameter and density distribution on the carbon black support.

Figure 2 illustrates a detailed characterization for C₂-Ag NPs. Transmission electron microscopy (TEM) image (Figure 2A) shows that C₂-Ag NPs have core sizes of ~10 nm. High-resolution TEM image (Figure 2B) and XRD data (Figure S3) indicate that these NPs possess a face-centered cubic Ag crystal phase. In the X-ray photoelectron spectroscopy (XPS) spectra (Figure 1C), the S 2p_{3/2} peak centered at 162.3 eV arises from thiol groups covalently bridged to the silver to form Ag-S-C links. Fourier Transformed Infrared Spectroscopy (FT-IR) spectrum (Figure 1d) confirms the presence of -NH₂ groups on C₂-Ag NPs.²⁷⁻²⁹ The detailed characterization for C₁₁-Ag and ligand-free Ag NPs are presented in Supporting Information (Figure S1-S3).

Figure 2. Characterization of C₂-Ag NPs. (A) TEM image (scale bar being 40 nm), (B) HRTEM image, (C) XPS spectrum, inset showing a high-resolution S 2p XPS spectrum, and (D) FT-IR spectrum.

We studied the chemisorption of CO₂ on C₂-Ag NP using *in situ* attenuated total reflectance infrared (ATR-IR) spectroscopy, which was taken at -0.6 V vs. RHE in 0.1 M NaHCO₃. As the purged gas is changed from Ar as CO₂, the first feature is the peak at 1409 cm⁻¹, attributed to chemisorbed CO₃²⁻ on the Ag surface,³⁰ which significantly decreases in intensity (Figure 3A), accompanied with two new peaks appearing at 1945 cm⁻¹ and 2343 cm⁻¹. The adsorption peak at 1945 cm⁻¹ stems from chemisorption of the CO reaction intermediate on Ag surface to form Ag-CO.^{30,31} The Peak of 2343 cm⁻¹ is from CO₂. Notably, as presented in Figure 2B, the peak at 1624 cm⁻¹, assigned to -N-H in-plane deformation, is shifted to a lower frequency of 1610 cm⁻¹ (Figure 3B). pH has little influence on this peak (Figure S8). Therefore, the ATR-IR peak shift is possibly associated with the appearance of reactive intermediate, in which case chemisorbed CO₂ is the most possible candidate. This shift suggests that there is a chemical interaction between NH₂ and CO₂ as well as the reaction intermediates. The peak locating at ~839 cm⁻¹, attributed to the CO₂ bonding with -NH₂, appears under the applied potential³², which further confirms the chemisorbing CO₂ taking place on C₂-Ag NPs during the electrolysis.

Figure 3. *In situ* ATR-IR spectra of C₂-Ag and C₁₁-Ag NPs at -0.6 V purged with Ar or CO₂. (A) And (C) the electrolyte is 0.1 M NaHCO₃ resolved in H₂O; (B) the electrolyte is 0.1 M NaHCO₃ resolved in D₂O. Because the δ_{HOH} bending mode of adsorbed water obscures the information of N-H bond and C=O bending, the experiment using D₂O to replace H₂O was carried out.

In contrast, the Ag-CO intermediate adsorption peak becomes negligible in the cases of C₁₁-Ag NP (Figure 3A) and ligand-free Ag NPs (Figure S4) as the CO₂RR catalysts. The difference on the ATR-IR spectra should be due to the lifetime variation of the intermediates. As presented in Figure 1, the chemically bonded intermediates are longer lived on the surface of cysteamine capped Ag NPs, which makes them detectable by ATR-IR. Upon extending the alkyl chain length from C₂ to C₁₁, the long alkyl chain inhibits the simultaneous interaction of CO₂ with Ag and NH₂ groups, because -NH₂ in C₁₁-Ag is far away from Ag surface and very possibly protonated to -NH₃⁺. This is supported by the ATR-IR spectra of C₁₁-Ag NPs in Figure 3B. The NH₂ peak of C₁₁-Ag NPs remains stationary at the electrolysis state. Furthermore, the

chemisorbed CO₂ peak at ~839 cm⁻¹ is undetectable in C₁₁-Ag NPs. All these suggest that the ligands assisting the chemisorption of CO₂ on Ag catalysts does not occur for C₁₁-Ag NPs.

Figure 4 shows the electrochemical CO₂RR activity of these Ag NPs. CO is the primary product for all three cases. The potential-dependent FEs of CO formation shows that for C₂-Ag NPs, significant amounts of CO are generated at an onset potential of -0.2 V, which is 0.09 V below the theoretical equilibrium potential of CO₂/CO (-0.11 V). The onset potentials for C₁₁-Ag NPs are shifted to -0.3 V. When ligands are removed from the surface, ligand-free Ag NPs require the highest onset potential of -0.5 V. The FE increases as the potential is increased. C₂-Ag NPs are the most active for CO formation with FE reaching 93% at -0.60 V. Extending the alkyl chain length to C₁₁ decreases the catalytic performance for CO₂RR. The CO partial current density of different NPs shown in Figure 4B. The electrochemical surface area is determined using lead underpotential deposition (UPD).³³ It can be found that C₂-Ag NPs possess the highest CO partial current density values at same conditions. The order of the catalytic activity for these Ag NPs is C₂-Ag > C₁₁-Ag > ligand-free Ag NPs. Compared to ligand-free Ag NPs, the C₂-Ag NPs can decrease the overpotential by 300 mV at 1 mA cm⁻². Taking -0.6 V as a reference potential, the turnover frequency (TOF) of C₂-Ag reaches 1.6 s⁻¹, which is ~10 fold better than that of C₁₁-Ag NPs (0.14 s⁻¹) and 53 times higher than that of ligand-free Ag NPs (0.03 s⁻¹) (Figure 4C). Meanwhile, the ligands possess high stability on Ag NPs even under the negative potential for CO₂RR (Figure S9-S10).

Figure 4. Influence of alkyl chain length on the CO₂ electroreduction catalysis. (A) FE for CO vs. potential; (B) CO partial current density vs. potential; (C) TOF for CO at -0.6 V; (D) stability of the C₂-Ag NPs characterized by FE for CO and total current density vs. time at -0.6 V.

This evaluation on CO₂RR indicates that thiolate ligands can improve the catalytic activity. But the significant difference in activity of C₂-Ag and C₁₁-Ag NPs suggests that the electron-localization effect due to the thiolate anchoring on Ag is not sufficient to explain this phenomenon. Our *in situ* ATR-IR combined with QM based molecular dynamics simulations indicates that the cis form of C₂ can further provide an extra stabilization effect by utilizing the terminal NH₂ forming HB bond with chemisorbed CO₂, which further reduces the overpotential. C₁₁ lacks of such ability because the carbon chain is too long leads to a significant hydrophobic nature that forces the ligand to fully extend. Thus, C₁₁-Ag NPs have less activity compared to C₂-Ag, but due to the electron-localization function, it is better than ligand-free Ag NPs. The synergistic combination of the assisted CO₂ chemisorption on Ag catalysts by -NH₂ with the

electron-localization effect endows the C₂-Ag NPs with superior high activity for CO₂RR compared to reported Ag-based catalysts (Table S1).

It has been found that cysteamine on noble metals can keep excellent stability even under a potential as -1.1 V vs. RHE.¹⁷ The synthesized C₂-Ag NPs exhibit superior stability in catalytic activity. Its total current density vs. time and CO FE vs. time at -0.6 V vs. RHE remain quite stable even after electrolysis for 10 hours (Figure 4D). The TEM image of the C₂-Ag NPs after 10-hour electrolysis shows almost no appreciable differences in the morphology (Figure S7).

Most important is that the promotion effect of surface ligands on catalysis is readily applied to enhance the catalysis of Ag foil. We immersed polished Ag foil into dilute cysteamine solution (5×10^{-6} mmol) for 10 min. Consistent with cysteamine on Ag NPs, the cysteamine self-assembled monolayer (SAM) coating on Ag foil enhances the catalytic activity and selectivity of CO₂ (Figure S8), decreasing the overpotential requirement for CO formation and increasing the CO partial current density. This experiment verifies that cysteamine SAM modification is a general approach to improving Ag electrodes for selective electroreduction of CO₂ towards CO.

In summary, our results demonstrate that thiolate SAM ligands can stabilize the chemisorbed CO₂ by geometrically and electron-dislocation effects to improve the catalytic activity of CO₂ electrochemical reduction markedly. Under the synergistic electron-dislocation and geometric CO₂ chemisorption effects, the NH₂ functionalized ligands of cysteamine decrease the overpotential by 0.3 V at 1 mA cm⁻², endowing the Ag NPs with 53-fold enhanced TOF and 9.3-fold increased FE for CO (reaching 93%) at -0.6 V vs. RHE. This finding provides new vista in inorganic material-based catalysis.

AUTHOR INFORMATION

Notes

The authors declare no competing financial interests.

ACKNOWLEDGMENT

T. C. and W. A. G. were supported by the Joint Center for Artificial Photosynthesis, a DOE Energy Innovation Hub, supported through the Office of Science of the U.S. Department of Energy under Award No. DE-SC0004993. This work used the Extreme Science and Engineering Discovery Environment (XSEDE) which is supported by National Science Foundation grant number ACI-1053575. Z. W. acknowledges financial support from the Open Project of State Key Laboratory of Urban Water Resource and Environment, Harbin Institute of Technology (No. HC201813). L. W. acknowledges financial support from the National Natural Science Foundation of China (No. 81771903) and Wuliande Foundation of Harbin Medical University (No. WLD-QN1404).

Supporting Information Available: Supporting Information includes Materials and Methods, Figures S1-S11 and Tables S1.

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