Silver Supported on Titania as an Active Catalyst for Electrochemical Carbon Dioxide Reduction

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Although significant research efforts have focused on the exploration of catalysts for the electrochemical reduction of CO₂, considerably fewer reports have described how support materials for these catalysts affect their performance, which includes their ability to reduce the overpotential, and/or to increase the catalyst utilization and selectivity. Here Ag nanoparticles supported on carbon black (Ag/C) and on titanium dioxide (Ag/TiO₂) were synthesized. In a flow reactor, 40 wt % Ag/TiO₂ exhibited a twofold higher current density for CO production than 40 wt % Ag/C. Faradaic efficiencies of the 40 wt % Ag/TiO₂ catalyst exceeded 90 % with a partial current density for CO of 101 mA cm⁻²; similar to the performance of unsupported Ag nanoparticle catalysts (AgNP) but at a 2.5 times lower Ag loading. A mass activity as high as 2700 mA mg⁻¹ Ag cm⁻² was achieved. In cyclic voltammetry tests in a three-electrode cell, Ag/TiO₂ exhibited a lower overpotential for CO₂ reduction than AgNP, which, together with other data, suggests that TiO₂ stabilizes the intermediate and serves as redox electron carrier to assist CO₂ reduction while Ag assists in the formation of the final product, CO.

Introduction

The world’s increasing energy consumption as a result of increases in the world population and increased energy consumption in developing parts of the world is accelerating the depletion of the world’s dwindling fossil-fuel reserves.[1] This increased energy consumption has led to a steady increase in atmospheric CO₂ levels over several decades, which in turn has been linked to undesirable climate change effects. To curb the rise, and eventually to lower the atmospheric CO₂ levels, multiple approaches need to be pursued because no single approach has the capacity to address this issue by itself.[2] Approaches to reduce CO₂ emissions include switching to energy sources that emit less CO₂ (e.g., natural gas instead of coal), carbon capture and sequestration from point sources such as power plants, enhancing the energy efficiency of buildings and cars, and the utilization of renewable sources such as solar and wind. Potential economic gains provide a natural incentive for the implementation of some of these approaches (e.g., enhancing the energy efficiency of buildings and cars), whereas other approaches will require regulation as they can only be implemented at a substantial cost (e.g., carbon capture and underground sequestration). Many renewable power plants (wind, solar, tidal, etc.) have become operational around the world but, because of their intermittent nature, these sources can only be used in combination with more conventional, fossil-fuel-based power plants. Furthermore, to avoid the waste of renewable power if the amount produced is high, methods for large-scale energy storage or on-demand utilization need to be developed.[3]

The catalytic conversion of CO₂ into useful chemicals such as intermediates for the synthesis of fuels and polymers by using photochemical, electrochemical, thermochemical, or other methods is another promising approach to curb atmospheric CO₂ levels, which provides the potential for economic gains at the same time.[4] More specifically, the electrochemical conversion of CO₂ into value-added products, such as formic acid, CO, hydrocarbons, or alcohols, can utilize on demand excess energy from renewable energy plants and help to reduce atmospheric CO₂ levels simultaneously.[5] However, significant improvements in the efficiency and at times the selectivity of the electrolysis of CO₂ into any of these products are needed for this process to become economically viable.[6, 7] Most electrocatalysts reported to date exhibit a high overpotential for the desired reaction, which drastically reduces the energy efficiency. Also, the conversion rate, as expressed by the observed current density, is still insufficient. Electrocatalysts need to be developed that simultaneously exhibit a low overpotential (thus...
high energy efficiency), high Faradaic efficiency (high selectivity), and high current density (thus high rate of conversion).\cite{7,12}

Over the past decades multiple metal catalysts have been tested for the production of various products by the electrochemical reduction of \( \text{CO}_2 \). For example, Hori et al. found that different metal catalysts exhibit selectivity for different products, that is, metals such as Ag and Au lead to predominantly CO, metals such as Sn lead to formate, and Cu leads to the formation of mixtures of hydrocarbons.\cite{9} Here, we focus on the conversion of \( \text{CO}_2 \) to CO as the combination of CO and \( \text{H}_2 \) (syngas) can be converted to liquid fuels through the Fischer–Tropsch process. Although some catalysts are able to produce \( \text{CO} \) and \( \text{H}_2 \) at the same time, we focus on catalysts that predominantly produce \( \text{CO} \) because \( \text{H}_2 \) can be obtained more efficiently (higher system efficiency and current density) from other sources, for example, water electrolysis, than by the co-generation of \( \text{H}_2 \) with CO. Overall, the optimization of the electrolysis cell for \( \text{CO}_2 \) production and the supply of \( \text{H}_2 \) from water electrolysis will be energetically more efficient than cogeneration in a single electrolyzer.\cite{5}

Some early work indicates that the large overpotential needed for \( \text{CO}_2 \) reduction mainly stems from the barrier of the initial electron transfer to form a \( \text{CO}_2^- \) intermediate that is poorly stabilized by most metal surfaces.\cite{14,16} Some approaches to stabilize this intermediate to lead to a lower overpotential have been reported. Recently, we reported the use of 1-ethyl-3-methylimidazolium tetrafluoroborate (EMIM-BF\(_4\)) as a cocatalyst in combination with an unsupported Ag-nanoparticle-based catalyst to lower the cell overpotential for the electroreduction of \( \text{CO}_2 \) to CO on Ag to \(-0.2 \text{ V, although at low current densities (<5 mA cm\(^{-2}\)) and high loading (6.67 mg of Ag per cm\(^2\))},\)\cite{11} Chen et al. reduced the overpotential of \( \text{CO}_2 \) reduction to CO to 140 mV by stabilizing the \( \text{CO}_2^- \) intermediate on the surfaces of oxide-derived Au electrodes.\cite{12} With respect to conversion, most studies that focus on the electroreduction of \( \text{CO}_2 \) to CO report current densities in the range of 2–118 mA cm\(^{-2}\) under ambient conditions, and most of these studies use Ag as the cathode catalyst.\cite{7} For example, Dufek et al.\cite{13} and Delacourt et al.\cite{14} reported partial current densities for CO \( j_{\text{CO}} \) of less than 60 mA cm\(^{-2}\) at \(-1.8 \text{ V vs. Ag/AgCl} \) if they operated their respective cells at ambient temperature and pressure. Tornow et al. studied N-based organometallic Ag catalysts, which achieved \( j_{\text{CO}} \) values as high as 115 mA cm\(^{-2}\) while the Ag loading was decreased by a factor of 20.\cite{15} Recently, we have reported that the performance of Ag catalysts in \( \text{CO}_2 \) reduction depends on the Ag nanoparticle size.\cite{16}

To date, significant efforts have focused on the exploration of catalysts, whereas significantly fewer studies have focused on the investigation of different catalyst supports. Catalyst supports can have tremendous influence on catalyst performance, which can result in lower catalyst loading.\cite{17} For example, in fuel cells, the reduction of the loading of precious catalysts, especially Pt, while increasing performance and durability, has been a critical step towards the improvement of the commercial viability of this technology.\cite{17} Specifically, support materials have been developed to support and stabilize smaller nanoparticles that are often more active to enable better catalyst dispersion and utilization and provide better electron conduction and mass transport.\cite{17,18}

\( \text{TiO}_2 \) has been used as a readily available support material and a catalyst for a variety of applications, which include as a noncarbonaceous support for Pt in fuel cell electrodes\cite{19} and as a catalyst itself in the photoreduction of \( \text{CO}_2 \).\cite{20} \( \text{TiO}_2 \) has been reported to interact strongly with Pt, which increases the Pt catalyst activity, stability, and durability.\cite{21,22} \( \text{TiO}_2 \) can also act as a redox electron carrier to facilitate various reduction reactions, which include \( \text{CO}_2 \) conversion.\cite{22} Additionally, the \( \text{TiO}_2 \) surface has been reported to assist in \( \text{CO}_2 \) adsorption,\cite{23} thus it may be able to stabilize the \( \text{CO}_2^- \) intermediate to reduce the overpotential.

Here we report the use of \( \text{TiO}_2 \) as a catalyst support for Ag catalysts to improve the reduction of \( \text{CO}_2 \) to CO. Previously, Cueto et al. observed the enhancement of \( \text{CO}_2 \) and/or \( \text{H}_2 \)O reduction with Ag particles (\(-250 \text{ nm}) that are electrodeposited onto a thin-film \( \text{TiO}_2 \) electrode.\cite{24} This work did not report product selectivity, and they did not study the role, if any, of the flat \( \text{TiO}_2 \) film. In contrast, the study reported here investigates the effect of much smaller, sub-10 nm Ag nanoparticles deposited on 15–30 nm \( \text{TiO}_2 \) particles on \( \text{CO}_2 \) electroreduction. Specifically, we synthesized and characterized two types of catalysts: different loadings of Ag catalyst supported on \( \text{TiO}_2 \) (Ag/\( \text{TiO}_2 \)) and 40 wt % Ag supported on carbon black (Ag/C). We compared their electrochemical performance in the reduction of \( \text{CO}_2 \) to CO with the performance of the well-studied Ag nanoparticle catalysts by using an electrochemical flow reactor.\cite{25,26} Through structural characterization and electrochemical experiments, we also investigated the role of the \( \text{TiO}_2 \) support in the enhancement of the catalytic sites, specifically with respect to its ability to maintain the Ag nanoparticles at their most catalytically active size and its ability to stabilize the \( \text{CO}_2^- \) intermediate.

**Results and Discussion**

**Composition analysis**

We synthesized catalysts composed of different amounts of Ag on a \( \text{TiO}_2 \) support and for comparison we also synthesized 40 wt % Ag on a carbon support (Vulcan XC-72R). Details of the synthesis of these catalysts are provided in the Experimental Section. The values for the actual Ag loading of the synthesized catalysts obtained by using inductively coupled plasma optical emission spectroscopy (ICP-OES) are summarized in Table 1. These values are in good agreement with the intended

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<tr>
<th>Catalyst</th>
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<td>5 wt % Ag/TiO(_2)</td>
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<tr>
<td>40 wt % Ag/C</td>
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**Table 1.** Ag composition of the synthesized catalysts.

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values except for the materials with low catalyst loadings, which can probably be explained by the relatively large loss of catalyst during the washing step as more frequent washing is required if a large amount of TiO₂ is added.

**Catalyst performance in the flow reactor**

**Performance comparison of different support materials**

The performance of the different Ag/TiO₂ and Ag/C catalysts was determined by using a flow reactor reported previously.[15, 25] We used 1 m KOH as the electrolyte as it has a higher conductivity than other commonly used electrolytes for CO₂ reduction, such as K₂SO₄ and KHCO₃.[26] The geometric area of the electrode was used to calculate current densities, j₂CO as a function of the cathode potential for four different cathode catalysts: 40 wt % Ag/TiO₂, 40 wt % Ag/C, AgNP, and plain TiO₂, which were immobilized on gas diffusion electrodes (GDE) by hand painting at an identical total cathode catalyst loading of 1 mg cm⁻², is shown in Figure 1 a. Ag/TiO₂ exhibits a better performance than Ag/C. Specifically, at −1.7 V vs. Ag/AgCl, j₂CO for 40 wt % Ag/TiO₂ was 60 mA cm⁻², whereas 40 wt % Ag/C reached 28 mA cm⁻². So at this cathode potential, approximately twice the amount of CO is produced by using TiO₂ rather than carbon black as the support material for the Ag particles. Then, at a cathode potential of −1.8 V vs. Ag/AgCl, the j₂CO observed for the 40 wt % Ag/TiO₂ catalysts was approximately 101 mA cm⁻², which is significantly higher than the value of approximately 62 mA cm⁻² reported previously for a commercially available ‘Silflon’ Ag GDE at the same cathode potential.[26] If the performance observed with 40 wt % Ag/TiO₂ is compared to the value reported by Cueto et al. who used 250 nm Ag particles on flat TiO₂ films, we observed that 40 wt % Ag/TiO₂ exhibited a much higher performance in terms of current density (two orders of magnitude higher) and selectivity for products from CO₂ conversion, although the current density reported by Cueto et al. is the sum of CO₂ conversion and H₂O reduction.[24] Also, the current density achieved with 40 wt % Ag/TiO₂ is ∼20 times higher than that achieved in our previous work,[15] but at a 15-times lower Ag loading: 0.4 vs. 6.67 mg of Ag per cm². The 40 wt % Ag/TiO₂ cathode and the AgNP cathode exhibit very similar performances (Figure 1 a). This result indicates that the Ag metal content can be drastically reduced without sacrificing performance if a Ag/TiO₂ catalyst is used, which improves its commercial viability for CO₂ reduction. The electrochemical surface area (ECSA) measurement of Ag described in the Supporting Information indicates that the ECSA of Ag in the 40 wt % Ag/TiO₂ electrode is much lower than the ECSA of Ag in the 40 wt % Ag/C or AgNP electrode, which underscores the important beneficial role of the TiO₂ support in the reduction of CO₂ and suggests the synergistic effect between Ag and TiO₂.

Interestingly, in the low current density regime, the 40 wt % Ag/TiO₂ cathode performed best (highest partial current density for CO₂), followed by the AgNP and 40 wt % Ag/C cathodes. This increased performance at low current density may be because of the increased adsorption of CO₂ and stabilization of \( \text{CO}_2^- \) by TiO₂. If plain TiO₂ was used as the cathode catalyst on a GDE (control experiment), no activity for CO production was observed, which confirms that the production of CO in the other experiments stems from the presence of Ag.

Single-electrode polarization curves for 40 wt % Ag/TiO₂, 40 wt % Ag/C, and AgNP are shown in Figure 1 b. The anode polarization curves are nearly identical because the same operating conditions, anode catalyst, and catalyst loading were used for all experiments. Therefore, the difference in total current densities can be attributed to differences in cathode performance. Naughton et al. developed a method to analyze polarization curves of individual fuel-cell electrodes by applying a linear fit in the Ohmic region to obtain a slope \( R_{\text{Ohmic}} \). A higher \( R_{\text{Ohmic}} \) value indicates a higher electrode resistance.
$R_{\text{Ohmic}}$ contains information about electrical resistances, any contact resistance between the electrolyte and electrode, and any mass transport losses. The $R_{\text{Ohmic}}$ parameter is not based exclusively on electrical resistance but rather is the apparent resistance in the Ohmic region. By using this method, we found that the lower performance of the Ag/C catalyst relative to the Ag/TiO$_2$ and AgNP catalysts was because of a higher resistance as indicated by a larger $R_{\text{Ohmic}}$ despite the fact that carbon black has a higher conductivity, which implies that in this case $R_{\text{Ohmic}}$ mainly originates from the contact resistance between the electrolyte and electrode as well as mass transport in both electrolyte and gas reactants rather than from the resistance caused by the low conductivity of support materials. Specifically, the carbon black support material is more hydrophobic and porous compared to the TiO$_2$ support material (Figure S2), which hampers contact between the Ag particles and the electrolyte. Also, compared to Ag/C, a thinner catalyst layer could be obtained for the Ag/TiO$_2$ catalyst at the same Ag loading because TiO$_2$ has a twofold higher density than carbon, which has improved mass transfer kinetics as previously reported.[19] The Faradaic efficiencies (see SI for details on the calculation) for CO, the desired product, and H$_2$, the byproduct, as obtained for GDEs covered with 40 wt% Ag/TiO$_2$, 40 wt% Ag/C, and AgNP catalysts, respectively, are shown in Figure 1c. Among these three catalysts, AgNP achieved the highest Faradaic efficiency for CO $>$ 95%. Ag/TiO$_2$ achieved a Faradaic efficiency for CO of 93%, whereas Ag/C achieved only 70% and much larger amounts of the byproduct H$_2$ were formed. Therefore, the low performance (i.e., the low partial current density) exhibited by Ag/C can be explained by its low Faradaic efficiency for CO, in addition to a higher electrode resistance (vide supra).

The effect of Ag loading on the Ag/TiO$_2$ performance

We also studied the performance of Ag/TiO$_2$ catalysts as a function of increasing Ag loading (5, 10, 20, 40, and 60 wt% Ag/TiO$_2$). Plots of the partial current density and Faradaic efficiency for CO versus the cathode potential for GDEs prepared with these catalysts with a constant total catalyst loading of 1 mg cm$^{-2}$ are shown in Figure 2a and b. In general (for the 5–40 wt% samples), the data indicated that the higher the Ag loading, the higher the partial current density and Faradaic efficiency for CO, especially at more negative cathode potentials (from $-1.5$ to $-1.8$ V vs. Ag/AgCl). TEM micrographs of the Ag/TiO$_2$ catalysts with different Ag loadings suggest that this trend can be explained by the increased number of Ag particles exposed on the TiO$_2$ surface (Figure 3). Interestingly, the 60 wt% Ag/TiO$_2$ catalyst did not follow this trend. Its partial current density and Faradaic efficiency for CO were much lower than those observed for the 40 wt% Ag/TiO$_2$ especially at negative cathode potentials. TEM images of the 60 wt% samples suggest that Ag particles are more prone to agglomerate than the 40 wt% sample during reaction (compare Figure 3e and e'), and histograms in Figure S4f and S4g) as the Ag particles are more densely arranged on the support in samples with a high loading, which increases the possibility for aggregation (compare Figure 3e and e'). The other possible reason for the lower performance of the 60 wt% sample is that according to the synergistic effect between Ag and TiO$_2$ (introduced later), an optimum Ag content, 40 wt% in this work, exists among the different Ag/TiO$_2$ catalysts. Catalysts with an Ag content higher or lower than 40 wt% exhibit a lower performance. Similar trends and explanations have been reported for other supported catalysts, for example, for Ag supported on carbon black in fuel-cell applications.[28]

One of the main advantages of the Ag/TiO$_2$ catalysts studied in this paper is their low mass fraction of Ag, which reduces the amount of precious metal needed. The performance per mass Ag (i.e., the mass activity) for all catalysts used in this study is compared in Figure 2c. For example, the mass activity of 5 wt% Ag/TiO$_2$ was 20-fold higher than that of the commercial AgNP catalyst and much higher than the mass activity of

![Figure 2](image-url)
N-based Ag catalysts (e.g., Ag pyrazole, AgPz), which we reported previously with a high mass activity of 1600 mA m\(^{-2}\) at –1.7 V vs. Ag/AgCl. In addition, all of the Ag/TiO\(_2\) catalysts showed relatively high cell energy efficiencies (see SI for details on the calculation). For example, the cell energy efficiency was 65% at a cell potential of –2 V for the 40 wt% Ag/TiO\(_2\) catalyst, compared to only 50% for the 40 wt% Ag/C catalyst and 56% for the AgNP catalyst.

### Ag particle size and size distribution

To explain the high performance of the GDEs covered with Ag/TiO\(_2\) catalysts in the flow reactor, we characterized the catalysts with respect to size and the size distribution of the nanoparticles supported by TiO\(_2\) or carbon black both before and after flow-reactor tests (Figure 3). The histograms of the Ag particle size distribution are shown in Figure S4. The synthetic method used here (see Experimental Section) yields more uniform and much smaller Ag particles that are at their active size (<10 nm) and dispersed well on the TiO\(_2\) (Figure 3a–e), especially if compared to the >200 nm electrodeposited Ag particles reported previously. However, for the Ag/C sample, both small (<10 nm) and large Ag particles (>100 nm) can be found on the carbon black (Figure 3f and g). Some of the Ag particles tend to agglomerate to yield larger Ag particles for metal loadings higher than 40 wt% (Figure 3d and e).

Catalyst activity in a standard three-electrode cell

The performance towards CO\(_2\) reduction for the Ag/TiO\(_2\) catalyst compared to the AgNP and Ag/C catalysts was also studied by using cyclic voltammetry (CV) in a standard three-electrode cell. K\(_2\)SO\(_4\) (0.5 M), a widely used electrolyte in CO\(_2\) reduction studies, was used here. In a standard three-electrode cell, KOH would react with CO\(_2\) to form carbonate/bicarbonate, which would, therefore, decrease the electrolyte pH significantly (from 13.58 to 9.96) and thus the amount of the active species, molecular CO\(_2\). However, we can use a KOH solution as the electrolyte in the flow reactor because once CO\(_2\) diffuses through the GDE, it reacts at the triple boundary phase to form CO, and the reaction of CO\(_2\) with KOH could be minimized. In fact, the flowing electrolyte will refresh the surface and minimize the pH decrease (from 13.65 to 13.48). Therefore, KOH can be used as an electrolyte to increase the electrolyte conductivity in the flow cell, and K\(_2\)SO\(_4\) is a better option than KOH in the three-electrode cell. Either CO\(_2\) or Ar gas was bubbled through the electrolyte for 15 min prior to CV measurements. As shown in Figure 4a, b, and c, extensive H\(_2\) evolution is observed on both the Ag and Ag/TiO\(_2\) electrodes in the Ar-saturated electrolyte. However, if we used a CO\(_2\)-saturated electrolyte, different reduction peaks with different onset potentials and lower peak currents, presumably associated with CO\(_2\) reduction, were observed for both catalysts. The smaller reduction peak current observed if a CO\(_2\)-saturated electrolyte
was used is probably because of the inhibition of the H₂ evolution reaction by the species that are adsorbed during CO₂ reduction.⁶ The Ag/TiO₂ catalyst (Figure 4 c) exhibits a 73 mV lower onset potential for CO₂ formation (and thus a lower overpotential) than the AgNP catalyst (Figure 4 a): 1.189 and 1.262 V vs. Ag/AgCl at i = 0.04 mA, and 102 mV lower onset potential for CO₂ formation than the Ag/C catalyst, respectively. The large overpotential typically observed for CO₂ reduction has been attributed to the barrier of the initial electron transfer to form a CO₂ intermediate, which is poorly stabilized by most metal surfaces.⁴ It is the improvement observed here may be because of the adsorption and stabilization of CO₂ on the TiO₂ surface. This may be further proved by the CV study shown in Figure S6 a, in which TiO₂ alone as a catalyst also exhibits a low onset potential of −1.196 V vs. Ag/AgCl for the conversion of CO₂ to CO₂ ads. This observation of an earlier onset potential for Ag/TiO₂ is also in agreement with the better performance of the Ag/TiO₂ catalyst compared to the AgNP catalyst in the lower current density regime and compared to the Ag/C catalyst in the whole current density range in the flow-reactor test (Figure 1 a). Therefore, both the experiments in the flow reactor and in the standard three-electrode cell with different electrolytes show that Ag/TiO₂ performs better than Ag/C and even pure AgNP.

Interestingly, another reduction peak at around −1.7 V vs. Ag/AgCl and two anodic peaks were also observed for the Ag/TiO₂ catalyst compared to the AgNP catalyst. To explain those peaks, Ar was bubbled into the solution for 3 min to remove some CO₂ after the CV scan was recorded in the CO₂-saturated electrolyte (Figure 4 c). The bubbling of Ar was repeated four times, and CV measurements were recorded each time after Ar was bubbled into the solution. As shown in Figure 4 d, if a relatively large amount of CO₂ was present in the electrolyte, two reductive (I and II) and oxidative peaks (III and IV) were observed. As the amount of CO₂ decreased, the intensities of peaks I and IV decreased, whereas that of peak III started to increase. The decrease in peak intensity indicates that peak I is related to the direct electrochemical reduction of CO₂ ads to CO₂ ads. The similar trend observed for peak IV is probably because of the oxidation of CO₂ ads. The other two peaks, II and III, can thus be attributed to the reactions for TiO₂ and Ti³⁺ species, which can indeed act as a redox electron carrier to facilitate some reactions, which include CO₂ reduction.⁶ There have been reports that the interfacial pH can be quite different from the bulk pH in unbuffered solutions, which affects the reaction rate.⁶ In this case, we did not use a buffered solution because we did not want the adsorption/desorption peaks from the anions in the buffer solution to interfere with any observed redox species. A similar experiment that used TiO₂ without Ag (Figure S6 a) confirms the redox behavior of Ti⁴⁺/Ti³⁺ for CO₂ ads reduction to CO₂ ads. Direct reduction of CO₂ by using TiO₂ as the catalyst is possible, however, a negligible amount of CO was observed if only TiO₂ was used, whereas Ag/TiO₂ is able to produce a much larger amount of CO in K₂SO₄ (0.5 m).
electrolyte in the flow reactor (Figure S6b), which indicates that the production of CO requires the presence of Ag on TiO₂.

A schematic that describes the proposed reaction pathway of the reduction of CO₂ on a Ag/TiO₂ catalyst is shown in Figure 5. CO₂ is first adsorbed on TiO₂. At less negative cathode potentials (more positive than the redox potential of the TiIV/TiIII couple), the adsorbed CO₂ gains one electron from the electrode and is converted to CO₂·ads. Then the produced CO₂·ads is adsorbed and stabilized on the TiO₂ surface, which results in a decrease of the overpotential for this step. At more negative cathode potentials, the TiIII species (which has been reported to form upon thermal annealing in a vacuum) is known to facilitate CO₂ adsorption, and can act as the active sites for CO₂ photoreduction in the presence of H₂O. The combination of the observation that TiO₂ alone is not able to produce CO as unsupported AgNP, but at a 2.5 times lower Ag loading. Furthermore, the 5 wt% Ag/TiO₂ catalyst achieved a mass activity as high as 2700 mA mg⁻¹ cm⁻². Ag is 5–10 times more expensive than TiO₂, therefore, supporting Ag particles on TiO₂ enhances the promise of these catalyst for the development of an economically viable process for the electrochemical reduction of CO₂ to CO.

We also studied the role of TiO₂ as a support material during the electrochemical reduction of CO₂. Based on cyclic voltammetry data, a reaction pathway is proposed that involves the participation of TiIV/TiIII from the support material, which acts as the redox couple and stabilizes the reaction intermediate. Further research is needed to confirm the proposed reaction pathway. For example, calculations and spectroscopic experiments could guide these efforts with respect to the prediction and confirmation of the adsorption/stabilization of intermediates and the interactions between metal particles and support materials.

Further studies could also focus on the exploration of other metal catalysts supported by metal oxide semiconductors such as CeO₂. Such catalysts may be able to modify the adsorption isotherms for the intermediates and be able to further decrease the energy barrier for the electrochemical reduction of CO₂.

**Experimental Section**

**Preparation of Ag/TiO₂ and Ag/C catalysts**

The previously reported citrate-protecting method was used to obtain the different Ag/TiO₂ catalysts. In contrast to previous reports, the support materials used here (TiO₂ or carbon black) were first mixed with AgNO₃ (40 mM; Sigma–Aldrich) aqueous solution to allow the better adsorption of Ag⁺ on the support. Sodium citrate (Fisher Chemicals) was then added to stabilize Ag⁺ followed by the addition of NaBH₄ (Sigma–Aldrich) to reduce Ag⁺. Specifically, for the synthesis of 40 wt% Ag/TiO₂, AgNO₃ (125.7 mg) was dissolved in Millipore H₂O (18.5 mL). TiO₂ (120 mg, Aerosil TiO₂, P25, particle size: 21 ± 5 nm) was added to the solution, and the mixture was stirred for 30 min. Subsequently, sodium citrate solution (131 mM, 18.5 mL) was added dropwise with stirring. The reduction of Ag⁺ was achieved by the dropwise addition of NaBH₄ solution (30 mM, 25 mL) with vigorous stirring in an ice bath. After stirring the solution gently overnight, it was centrifuged, washed, and dried in a vacuum oven at 80 °C for 4 h. The obtained catalyst was white in color. Samples with Ag loadings of 5, 10, 20, and 60 wt% were prepared by using the same method by changing the amount of TiO₂. For comparison, 40 wt% Ag/C catalyst was prepared in the same way.
synthesized with the same method by using Vulcan XC-72R (Carbon Blk Vulcan XC-72R, Fuel Cell Store) as the support.

**Physical characterization**

The Ag weight percentages of the different catalysts were determined by using ICP-OES (PerkinElmer-Optima 2000DV). The samples were digested in a mixture of HNO₃ and HF prior to analysis. The Ag particle size and dispersion on the support were examined by using TEM (JOEL 2100 CRYO) operated at 200 kV. The TEM sample was prepared by suspending the catalyst in isopropanol and placing a drop of the suspension onto a holey carbon-coated 200 mesh grid followed by solvent evaporation overnight at RT.

**Electrochemical characterization**

**Electrode preparation**: Catalyst inks were prepared by mixing Millipore water (200 µL), catalyst (2 mg), Nafion solution (2.6 µL, 5 wt%, Fuel Cell Earth), and isopropyl alcohol (200 µL). The inks were then sonicated (Vibra-Cell ultrasonic processor, Sonics & Materials) for 15 min and then painted on the microporous layer of Sigracet 35 BC gas diffusion layers (Ion Power) with a paintbrush. All of the flow-reactor experiments in this study used a 1 mg cm⁻² cathode catalyst loading on Sigracet 35BC, and all of the anodes used in this study had a 1 mg cm⁻² Pt loading on Sigracet 35BC.

**Electrochemical flow reactor operation**: The flow reactor (see SI for a schematic) was operated under ambient conditions. A potentiostat (Autolab PGSTAT302N, EcoChemie) operating in steady-state chronoamperometric mode was used to measure the resulting current as reported previously.⁶ For each trial, five cell potentials from −2.0 to −3.0 V with an interval of 0.25 V was applied to the cell. For each potential, the cell was allowed to reach steady state for 200 s, after which the gas flowed into a gas chromatograph. The current was averaged for an additional 180 s before stepping to the next potential. The individual electrode potentials were measured by using multimeters (AMPROBE 15XP-B) connected to the next potential. The individual electrode potentials were measured by using multimeters (AMPROBE 15XP-B) connected to the next potential. The individual electrode potentials were measured by using multimeters (AMPROBE 15XP-B) connected to the next potential. The individual electrode potentials were measured by using multimeters (AMPROBE 15XP-B) connected to the next potential.

**Three-electrode cell operation**: CVs were measured by using a standard three-electrode cell, which consisted of a Pt gauze (100 mesh, 99.9% metals basis, Sigma–Aldrich, 25×25 mm²) counter electrode and a Ag/AgCl reference electrode (RE-SB, BAS®) placed in the exit stream. A mass flow controller (MASS-FLO, MKS Instruments) was used to flow CO₂ from a cylinder at 7 sccm. A syringe pump (PHD 2000, Harvard Apparatus) supplied the 1 µ KOH electrolyte at 0.5 mL min⁻¹. Gas products that formed on the GDE surface left through the GDE to the gas stream driven by a vacuum connected to the end of the gas channel. For the composition analysis of H₂ and CO₂, the effluent gas stream flowed directly into a gas chromatograph (Thermo Finnegan Trace GC) operating in the thermal conductivity detection (TCD) mode, with a Carboxen 1000 column (Supelco) and He as the carrier gas at a flow rate of 20 sccm. The column was held at 150 °C, and the TCD detector was held at 200 °C. The only cathode products detected by GC may have formed as well but only in very small amounts (<4 % for 40 wt% Ag/TiO₂ and AgNP; <10% for 40 wt% Ag/C). The results of these minor products were beyond the scope of this study. After each trial to test 40 wt% Ag/TiO₂ and 60 wt% Ag/TiO₂, the catalysts were further characterized by TEM.

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