Time-Resolved IR Spectroscopy Reveals a Mechanism with TiO₂ as a Reversible Electron Acceptor in a TiO₂–Re Catalyst System for CO₂ Photoreduction

Mohamed Abdellah,†§ Ahmed M. El-Zohry,† Liisa J. Antila,† Christopher D. Windle,§ Erwin Reisner,§* and Leif Hammarström†§*

†Ångström Laboratory, Department of Chemistry, Uppsala University, Box 523, 75120 Uppsala, Sweden
‡Department of Chemistry, Qena Faculty of Science, South Valley University, 83523 Qena, Egypt
§Christian Doppler Laboratory for Sustainable SynGas Chemistry, Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge CB2 1EW, United Kingdom

ABSTRACT: Attaching the phosphonated molecular catalyst [ReBr(bpy)–(CO)₃]⁰ to the wide-bandgap semiconductor TiO₂ strongly enhances the rate of visible-light-driven reduction of CO₂ to CO in dimethylformamide with triethanolamine (TEOA) as sacrificial electron donor. Herein, we show by transient mid-IR spectroscopy that the mechanism of catalyst photoreduction is initiated by ultrafast electron injection into TiO₂, followed by rapid (ps–ns) and sequential two-electron oxidation of TEOA that is coordinated to the Re center. The injected electrons can be stored in the conduction band of TiO₂ on an ms-s time scale, and we propose that they lead to further reduction of the Re catalyst and completion of the catalytic cycle. Thus, the excited Re catalyst gives away one electron and would eventually get three electrons back. The function of an electron reservoir would represent a role for TiO₂ in photocatalytic CO₂ reduction that has previously not been considered. We propose that the increase in photocatalytic activity upon heterogenization of the catalyst to TiO₂ is due to the slow charge recombination and the high oxidative power of the ReII species after electron injection as compared to the excited MLCT state of the unbound Re catalyst or when immobilized on ZrO₂, which results in a more efficient reaction with TEOA.

INTRODUCTION

Tremendous efforts have been put toward exploring new energy resources to face the problems of energy shortage and global warming. A continuous increase of the CO₂ concentration in the atmosphere is the main reason behind global warming.¹ A smart solution is to convert CO₂ emissions to fuels or other useful chemicals, which is one of the goals of artificial photosynthesis.²−¹⁰ Photocatalytic and photoelectrocatalytic reduction of CO₂ has been achieved by employing metals and semiconductors¹¹−¹³ or enzymes bound to photoelectrodes.¹⁴,¹⁵ The former suffers from poor selectivity, and conversely, the latter shows excellent selectivity but suffers from stability issues.¹⁴,¹⁵ Balancing between both high selectivity and stability can potentially be achieved using a synthetic molecular catalyst for CO₂ reduction.⁷,¹⁰,¹¹,¹⁶−¹⁹ Generally, there are two approaches to CO₂ photoreduction with synthetic molecular catalysts. In the first, the catalyst receives electrons from a photosensitizer after excitation. In the second, the catalyst itself plays a dual role, working as both photosensitizer and catalyst as exemplified by the rhenium tricarbonyl bipyridine bromide [ReBr(bpy)(CO)₃]¹⁰ catalyst (Figure S1A).⁵,¹⁰

Recently, some of us attached this catalyst to an n-type TiO₂ semiconductor via phosphonic acid linker groups (TiO₂ – [Re(2,2′-bipyridine-4,4′-bisphosphonic acid)(CO)₃(L)], where initially L = Br⁻ but is replaced during the photoreaction; Scheme 1). In the presence of triethanolamine (TEOA) as electron donor, this leads to a higher yield (TON) of CO₂ photoreduction compared to both the homogeneous system without TiO₂ and to systems where the same catalyst was attached to other metal oxides, such as ZrO₂. Twenty TiO₂ was proposed to stabilize reduced catalyst intermediates and hinder formation of unreactive Re–Re dimers but not participate directly in the electron transfer reactions.

In the present study, we attempt to answer several questions to understand the role of TiO₂ and to propose the photoreduction mechanism of the attached catalyst. First, is TiO₂ unreactive or is the excited [ReBr(bpy)(CO)₃] oxidized by electron injection into TiO₂ as has been shown in some cases?²² Second, what are the roles of the TEOA in the photocatalytic process? Finally, what is the role of TiO₂ in the photoreduction process? To answer these questions, we used

Received: October 31, 2016
Published: December 24, 2016

DOI: 10.1021/jacs.6b11308
J. Am. Chem. Soc. 2017, 139, 1226−1232
time-resolved IR (TRIR) in the region of CO stretching vibrations from time scales of femtoseconds up to seconds. \( \nu(^1\text{CO}) \) is very sensitive to the electron density of the central Re ion, allowing us to identify and follow the Re excited state and different oxidation states.23–25

\[ \text{Scheme 1. Ligand Exchange Process Combined with CO}_2 \text{ Capture of the } [\text{Re}^1(^{bpy})(\text{CO})_3\text{DMF}]^+ \text{ Catalyst in TEOA/CO}_2 \text{ Solution} \]

TiO\(_2\) [TiO\(_2\)], TEA \[\text{TEOA} \]

For the spectroscopy measurements, 2 mg of the catalyst was dissolved in 10 mL of DMF; then, mesoporous TiO\(_2\) (anatase nanoparticles with average size \(\sim 20 \text{ nm} \)) and bandgap \(\sim 3.2 \text{ eV} \) films were immersed in this solution for the sensitization process for 20 h while the photocatalytic activity was carried out for the colloidal TiO\(_2\)-catalyst hybrid system.21 The catalyst has a broad MLCT band at \(\Delta = 380 \text{ nm} \) followed by an ultraviolet band below 350 nm due to ligand-centered transitions.29 The MLCT band stays the same after the attachment to TiO\(_2\) (Figure S1B).24 The MLCT state generates a characteristic broad emission band at \(\Delta = 600 \text{ nm} \) for the triplet state \((\text{Re})^*\) (see inset of Figure S1B). The FTIR spectrum for TiO\(_2\)-[Re\(^{bpy}(\text{CO})_3\text{DMF}]^+ \) on CaF\(_2\) films were measured directly using the same setup. For the ligand exchange to be monitored in the presence of TEOA and CO\(_2\), the attached catalyst on TiO\(_2\) films (on CaF\(_2\)) was immersed into a DMF/TEOA (S:1) mixture with continuous CO\(_2\) bubbling.

\[ \text{Ultrafast Transient Mid-IR Absorption Spectroscopy.} \]

The 1 mJ, 45 fs output of a 1 kHz Ti:sapphire amplifier (Spitfire Pro, Spectra-Physics) was split into two separate commercial optical parametric amplifiers (TOPAS-C, Light Conversion), which generate the visible pump at 418 nm and the mid-IR probe (1850–3850 cm\(^{-1}\)) in DMF was corrected for the wavelength-dependent instrument sensitivity and measured at the right angle using a 1 cm quartz cuvette. IR spectra for [Re\(^{bpy}(\text{CO})_3\text{DMF}]^+ \) in DMF was recorded in a modified Omni cell (Specac) with O-ring sealed CaF\(_2\) windows and a path length of 100 \(\mu\text{m} \) using a Bruker IFS 66v/S FTIR spectrophotometer controlled by OPUS software. IR spectra for TiO\(_2\)-[Re\(^{bpy}(\text{CO})_3\text{DMF}]^+ \) on CaF\(_2\) films were measured directly using the same setup. For the ligand exchange to be monitored in the presence of TEOA and CO\(_2\), the attached catalyst on TiO\(_2\) films (on CaF\(_2\)) was immersed into a DMF/TEOA (S:1) mixture with continuous CO\(_2\) bubbling.

\[ \text{Steady-State Spectroscopy.} \]

Steady-state absorption and emission were recorded using a Varian Cary 5000 and a Horiba Jobin Yvon Fluorolog, respectively. The emission spectrum for [Re\(^{bpy}(\text{CO})_3\text{DMF}]^+ \) in DMF was corrected for the wavelength-dependent instrument sensitivity and measured at the right angle using a 1 cm quartz cuvette. IR spectrum for [Re\(^{bpy}(\text{CO})_3\text{DMF}]^+ \) in DMF was recorded in a modified Omni cell (Specac) with O-ring sealed CaF\(_2\) windows and a path length of 100 \(\mu\text{m} \) using a Bruker IFS 66v/S FTIR spectrophotometer controlled by OPUS software. IR spectra for TiO\(_2\)-[Re\(^{bpy}(\text{CO})_3\text{DMF}]^+ \) on CaF\(_2\) films were measured directly using the same setup. For the ligand exchange to be monitored in the presence of TEOA and CO\(_2\), the attached catalyst on TiO\(_2\) films (on CaF\(_2\)) was immersed into a DMF/TEOA (S:1) mixture with continuous CO\(_2\) bubbling.

\[ \text{RESULTS AND DISCUSSION} \]

Electron Injection from Excited [Re\(^{bpy}(\text{CO})_3\text{DMF}]^+ \) to TiO\(_2\). To investigate the electron injection from the excited catalyst [Re\(^{bpy}(\text{CO})_3\text{DMF}]^+ \) to TiO\(_2\), we first used the same sensitization conditions to attach the catalyst to ZrO\(_2\) (noninjecting semiconductor as a reference).31 Then, we used fs-TRIR to test the electron injection process. The ZrO\(_2\)-[Re\(^{bpy}(\text{CO})_3\text{DMF}]^+ \) system shows the typical spectral features of the excited [Re\(^{bpy}(\text{CO})_3\text{DMF}]^+ \); the bleach of the ground state CO bands (GSB) at \(\sim 2040 \text{ cm}^{-1} \) and around 1960 cm\(^{-1}\) and the corresponding excited-state bands (ESA) at \(\sim 2057 \text{ cm}^{-1} \) and around 2010 cm\(^{-1}\) (Figure 1A).22 In addition to these spectral features, the TiO\(_2\)-[Re\(^{bpy}(\text{CO})_3\text{DMF}]^+ \) system shows (i) a new peak on the higher wavenumber side compared to the ground state bleach (GB) due to the oxidized state of the catalyst [Re\(^{bpy}(\text{CO})_3\text{DMF}]^{2+} \) at \(2088 \text{ cm}^{-1} \) (Figure 1B) and (ii) a broad absorption band in the entire probe region due to electrons in the TiO\(_2\) conduction band \((\text{CB})\) (Figure 1C). The amplitude of both the oxidized catalyst [Re\(^{bpy}(\text{CO})_3\text{DMF}]^{2+} \) peak and the electrons in the TiO\(_2\) CB increase with increasing delay time with no decay up to 5 ns. Thus, there is no observable charge recombination on this time scale, but instead, there is a slow additional component of electron injection. The traces at 2088 cm\(^{-1}\) (oxidized catalyst after background subtraction of e\(^{-}\)\text{CB} \) signal) and at 2125 cm\(^{-1}\) (e\(^{-}\)\text{CB} \) signal) have different kinetics (Figure 2B). The electron trace shows significant appearance of the e\(^{-}\)\text{CB} \) signal on an \(\sim 2 \text{ ps} \) time scale, whereas the oxidized catalyst peak growth is slower (\(\sim 30 \text{ ps} \)). This difference could be because the electron signal is very strong and initially buries the oxidized catalyst peak. The catalyst peak is initially broad
but narrows with time and is thus more clearly seen as has been observed before.\textsuperscript{22,32,33} The spectral narrowing occurs on \(~30\) ps time scale. In separate experiments using ns-laser excitation with a cw-IR laser probe, we found that the electrons recombine on the tens of \(\mu\)s time scale (Figure S2A).

**The Role of TEOA.** TEOA is not just an external (outer-sphere) electron donor in DMF solutions. Instead, under illumination in the presence of TEOA, the \([\text{Re}(\text{bpy})(\text{CO})_3\text{DMF}]^+\) catalyst binds \(\text{CO}_2\) in the form of a \(\text{bpy}^-\) catalyst bound \(\text{CO}_2\) with \(\text{bpy}^-\) in a high wavenumber side of the GSB is absent, whereas the electrons are clearly present in the CB of TiO\(_2\). Thus, the TEOA-ligand seems to be able to reduce the oxidized catalyst on the same time scale as the electron injection process, forming the species where the “hole” has moved to the TEOA ligand: \(\text{TiO}_2(e^-)-[\text{Re}(\text{bpy})(\text{CO})_3\text{OC}(\text{O})\text{O}-(\text{CH}_2)_2\text{NR}_2]^+\). Figure 1C shows the TRIR spectra of \(\text{TiO}_2-\text{[Re}(\text{bpy})(\text{CO})_3\text{OC}(\text{O})\text{O}-(\text{CH}_2)_2\text{NR}_2]^+\) where the \(e^-\) signal on the lower wavenumber side has been subtracted to emphasize the molecular signals.

The reactions were followed on a longer time scale using a ns-laser/TRIR setup. Figure 2 compares the TRIR spectra of \(\text{TiO}_2-[\text{Re}(\text{bpy})(\text{CO})_3\text{DMF}]^+\) without (2A) and with (2B) TEOA and \(\text{CO}_2\). At first sight, in Figure 2A, we can recognize the GSB peak and the oxidized catalyst peak \(\text{TiO}_2(e^-)-[\text{Re}(\text{bpy})(\text{CO})_3\text{DMF}]^2+\) on the higher wavenumber side, which agrees well with the fs-FTIR results of Figure 1A. These signals decay on a time scale of a few \(\mu\)s. In contrast, after introducing TEOA and \(\text{CO}_2\) we found that, in addition to the GSB of \(\text{TiO}_2(e^-)-[\text{Re}(\text{bpy})(\text{CO})_3\text{OC}(\text{O})\text{O}-(\text{CH}_2)_2\text{NR}_2]^+\) at \(2020\) cm\(^{-1}\), an absorption peak appears on the lower wavenumber side, and this grows stronger during the first few 100s of ns. This means an increased electron density on the Re center and can be attributed to a singly reduced catalyst.\textsuperscript{34,35} Our assignment is based on the following spectral analysis. We subtract the spectrum at \(50\) ns from the spectrum at \(5000\) ns for the TiO\(_2\)-catalyst samples with and without TEOA/\(\text{CO}_2\) (Figure S3F). The resulting peak at \(2015\) cm\(^{-1}\) for the sample with TEOA/\(\text{CO}_2\) is in good agreement with the results of Kubiak and co-workers,\textsuperscript{34} who reported the FTIR spectrum of the singly reduced species \([\text{bpy}^-\text{bpy}^-\text{CO}_2\text{ReCl}^-]+\) (\(\text{bpy}^-\text{bpy}^- = 4,4',\text{di-tert-butyl}2,2',\text{bipyridine}\)), where the added electron density centered mostly on the bipyridine ligand.\textsuperscript{34} The electron density on the Re center induced by the anionic Cl\(^-\) ligand in their work is matched by the carbonate ligand in the present case. The doubly oxidized TEOA (\(\text{R}_2\text{-N}-(\text{CH}_2)_2\text{OH}\)) is formed via deprotonation and rearrangement to the corresponding \(\text{R}_2\text{N}^- = \text{CH}_2\text{OC}(\text{O})\text{O}^-\) species. Thus, we propose the structural notation \(\text{TiO}_2(e^-)-[\text{Re}(\text{bpy})(\text{CO})_3\text{OC}(\text{O})\text{O}-(\text{CH}_2)_2\text{NH}^+\text{R}_2]^+\) for the reduced catalyst species from which one proton has been released. Note that the formation of the singly reduced catalyst is not at the expense of the electrons in the TiO\(_2\) CB as the entire background absorption increases on the same time scale (Figure 2B). The only plausible electron source for catalyst reduction is the oxidized TEOA.
radical \([\text{OC(O)}\text{O(\text{CH}_2\text{CH}_2\text{N}+\text{R}_2)}]^-\) that is unstable and highly reducing, such that each TEOA can donate two equivalents of electrons.\(^{36-39}\) On ZrO\(_2\) instead, there was no measurable formation of the singly reduced catalyst on this time scale (Figure S3F). This finding confirms that electron injection from \([\text{Re}^+\text{(bpy)}\text{(CO)}_3\text{OC(O)}\text{O(\text{CH}_2\text{CH}_2\text{N}+\text{R}_2)}]^-\) into TiO\(_2\) plays a role in the photoreduction process. This triggers the first oxidation of TEOA on a ps time scale and releases a second equivalent of electrons on a time scale of \(\sim 1\ \mu s\). The second equivalent mostly reduces the Re catalyst but some apparently ends up as CB electron. This can possibly be explained by the close proximity of the re-coordinated TEOA to TiO\(_2\) or by prior decoordination of the TEOA radical from the Re complex. Thermodynamically, the TEOA radical has enough reducing power to reduce the Re complex, and consequently, it is able to reduce the CB of TiO\(_2\).\(^{37}\) Figure 3A compares the traces at 2015 cm\(^{-1}\) for the singly reduced catalyst TiO\(_2\)\((e^-)\)\([\text{Re}^+\text{(bpy)}\text{(CO)}_3\text{OC(O)}\text{O-C\text{H}_2\text{CH}_2\text{N}+\text{R}_2)}]^-\) that is unstable and highly reducing, such that each TEOA can donate two equivalents of electrons.\(^{36-39}\)

1.8\(\mu s\). At the same time the background signal of CB electrons increases for which the IR extinction coefficient is larger than for the catalyst species (see the relative \(\Delta\text{Abs}\) of the molecular peak vs broad background in Figure 2B).

**TiO\(_2\) Role in CO\(_2\) Photoreduction by [Re\(^+\text{(bpy)}\text{(CO)}_3\)]\(^+\)**

Catalyst. The data indicate that there is an electron injection from the excited [Re\(^+\text{(bpy)}\text{(CO)}_3\text{L})^*\] to the TiO\(_2\) CB on a ps time scale. For the sample with TEOA/CO\(_2\), this leads to phototriggered oxidation of TEOA and formation of a reduced catalyst, which is not seen on ZrO\(_2\). Therefore, TiO\(_2\) has an active role in the light-induced electron transfer reactions of this system. To further investigate the role of TiO\(_2\), we probed the destiny of CB electrons on longer time scales. Figure 3B compares the traces at 2100 cm\(^{-1}\) (CB electron absorption region) up to 1.5 s after photoexcitation of the TiO\(_2\) catalyst without (red trace) and with introducing TEOA/CO\(_2\) (black trace). Without TEOA/CO\(_2\), no electrons were left in the TiO\(_2\) CB on this time scale, but introduction of TEOA/CO\(_2\) to the attached catalyst changed the kinetics drastically. Clearly, the electrons were still in the TiO\(_2\) CB on this time scale, and only around 50% of the electrons had disappeared from the CB after around 100 ms, whereas the remaining 50% decayed with \(\tau \approx 1\ s\). This time scale (\(\tau \approx 1\ s\)) is very similar to that reported for decay of the reduced catalyst signal (\(\tau \approx 0.4\ s\)) at 500 nm (bpy-Re signal)\(^{21}\) even though we could not follow the molecular signal by mid-IR on the ms to seconds time scale. It is important to note that there is no accumulation of more reduced catalyst species upon repeated laser flashing or continuous irradiation. Thus, we propose that the CB electrons
are added to the reduced catalyst and lead to catalytic turnover, restoring the sample to the initial TiO$_2$−[Re(I)(bpy)(CO)$_3$-OC(O)O-(CH$_2$)$_2$NR$_2$]$^0$ state; we discuss a possible mechanism in the next section. At present, we do not know if the CB electrons that decay with $\tau \approx 89$ ms also contribute to catalyst reduction or if they are lost in side reactions. In any case, these experiments add more evidence that TiO$_2$ plays a role in the photocatalytic reduction of CO$_2$ in this system other than being a scaffold. In this context, we note again that formation of the singly reduced catalyst [Re(I)(bpy)(CO)$_3$−OC(O)O-(CH$_2$)$_2$NR$_2$]$_0$ on ZrO$_2$, by quenching of the excited Re complex by the appended TEOA was not measurable (Figure S3F), which means that the electron injection process in TiO$_2$ promotes formation of this species. This agrees well with the differences in catalytic activity of the catalyst on TiO$_2$ and on ZrO$_2$.\textsuperscript{21}

**Proposed Photocatalytic Mechanism.** The mechanism of CO$_2$ reduction by [Re(I)(bpy)(CO)$_3$L] catalysts is still under debate with different mechanistic pathways being discussed.\textsuperscript{35,40,41} Under electrocatalytic reduction conditions, the complex typically undergoes a two-electron reduction and loses the labile ligand (L) to form a [Re(bpy)(CO)$_3$]$_2^+$. \textsuperscript{41} This complex is more reducing than the CO complex and therefore undergoes electron transfer with TiO$_2$ to form CO$_2$ and start the catalytic cycle.\textsuperscript{42} Attaching the catalyst to TiO$_2$ improves the catalytic activity but also further increases the mechanistic complexity. Scheme 2 presents our proposed mechanism of the photocatalytic reduction of CO$_2$ using the TiO$_2$−[Re(I)(bpy)(CO)DMF]$^0$ system in the presence of TEOA/CO$_2$ in DMF solution. As shown above, TiO$_2$−[Re(I)(bpy)(CO)$_3$]$^+$ is able to capture CO$_2$ and bind it as a carbonated TEOA ligand, forming the catalyst TiO$_2$−[Re(I)(bpy)(CO)$_3$−OC(O)O-(CH$_2$)$_2$NR$_2$]$_0$. Upon photoexcitation of this complex, electron injection into the CB of TiO$_2$ occurs on the ps time scale. This is rapidly followed by electron transfer from the bound TEOA ligand [-(CH$_2$)$_2$NR$_2$] to the oxidized catalyst to form TiO$_2$(e$^-$)−[Re(I)(bpy)(CO)$_3$−OC(O)O-(CH$_2$)$_2$NR$_2$]$^0$. On a ns–µs time scale, the (-(CH$_2$)$_2$NR$_2$)$^{•+}$ radical cation shifts the radical from the nitrogen to an adjacent carbon that deprotonates and donates a second electron to further reduce the complex and form TiO$_2$(e$^-$)−[Re(I)(bpy)(CO)$_3$]−(CO)$_2$−OC(O)O-(CH$_2$)$_2$NR$_2$$^+$ + H$. This must be followed by release of the oxidized TEOA to form the CO$_2$-bound catalyst TiO$_2$(e$^-$)−[Re(I)(bpy)(CO)CO$_2$]$^0$, where the CO$_2$ now coordinates to the Re center and two reducing equivalents are located on the CO$_2$ group. The CO$_2$ may be derived from the carbonate-TEOA ligand that loses TEOA and rearranges to carbon coordination. Alternatively, the entire ligand decoordinates to form the one-electron-reduced, 17-electron species TiO$_2$(e$^-$)−[Re(I)(bpy)(CO)$_3$]$_0$ that then binds another CO$_2$ molecule. Both pathways end up forming the critical TiO$_2$(e$^-$)−[Re(I)(bpy)(CO)$_3$]$_0$ species. On a time scale of ms to seconds, electrons in the CB of TiO$_2$ reduce [Re(I)(bpy)(CO)CO$_2$]$^0$ to form the metallocarboxylate intermediate species TiO$_2$−[Re(I)(bpy)(CO)$_3$]−. The metallocarboxylate intermediate can undergo a protonation (from TEOA/DMF) followed by loss of H$_2$O to generate TiO$_2$−[Re(I)(bpy)(CO)CO$_2$]$^−$. This 18-electron species must be reduced before CO is released and the starting complex is regenerated. The question is where does this final electron come from under our experimental conditions. On the basis of results from Kubiak and co-workers,\textsuperscript{35} we suggest that a small fraction of electron equivalents from the TiO$_2$ CB could catalytically reduce the entire population of [Re(I)(bpy)-(CO)$_3$]$_0$.

Kubiak and co-workers found that substoichiometric amounts (~0.1 equiv) of reductant were sufficient to convert an entire sample of [Re(I)(bpy)(CO)$_2$]$^0$ to [Re(I)(bpy)-(CO)$_3$]$_0$ in homogeneous solution. They presented a mechanism with an electron-transfer-catalyzed ligand exchange.\textsuperscript{35} Formation of TiO$_2$−[Re(I)(bpy)(CO)$_2$]$^0$ in a small amount leads to replacement of CO with solvent molecule (DMF) to form TiO$_2$−[Re(I)(bpy)(CO)DMF]$^0$. This complex is more reducing than the CO complex and therefore undergoes electron transfer with TiO$_2$−[Re(I)(bpy)-(CO)DMF]$^+$ to propagate the reduction-ligand exchange process according to the small loop presented in Scheme 2.\textsuperscript{35} Finally, TiO$_2$−[Re(I)(bpy)(CO)DMF]$^+$ binds TEOA and CO$_2$ to reform the starting material as it was before laser flash initiation. Note that the scheme does not indicate all possible charge recombination steps and other loss pathways, which presumably make the overall quantum yield much less than 100%. The most interesting part of the proposed mechanism is that the catalyst is able to inject electrons to TiO$_2$, and when the catalyst becomes reduced by TEOA, it can accept the electron back. This explains the redox active role of TiO$_2$ as an electron reservoir in the TiO$_2$ catalyst system in the presence of TEOA and CO$_2$.\textsuperscript{89 ms}

**Scheme 2. Proposed Photocatalytic Mechanism of the [Re(I)(bpy)(CO)$_3$]$_0$ Catalyst Attached to the TiO$_2$ Surface for CO$_2$ Reduction**

\textsuperscript{8}The states formed on the ps–µs time scale were spectroscopically observed (above the dashed line), whereas the remaining species (below the dashed line) are suggested based on published mechanisms to complete catalytic turnover (see text). For simplicity of notation, we ignore the (CO)$_3$ groups in the catalyst chemical structure in this scheme.
CONCLUSIONS

We have shown that TiO2 plays an important and active role in the photocatalytic reduction of CO2 by the [Re(I)(bpy)(CO)3L] catalyst in DME and TEOA. First, the electron injection from the excited catalyst to TiO2 is followed by rapid and efficient regeneration of the ReI center by the attached TEOA ligand. A second electron transfer from the TEOA radical cation, leads to formation of the singly reduced [ReI(bpy−)(CO)3L] species on a time scale of 35 ns. We propose that the increase in photocatalytic activity observed when the catalyst is bound to TiO2, as compared to ZrO2 or in homogeneous solution, is due to the slow charge recombination and high oxidative power of the ReI species after injection as compared to the excited MLCT state on ZrO2 or in solution, which results in a more efficient reaction with TEOA. Second, it seems that TiO2 works as an electron bank that is able to accept, save, and give back the electrons to the catalyst and thus to help complete the photochemical reduction of CO2.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.6b11308.

Steady-state absorption, emission, IR spectroscopy, and complementary time-resolved IR spectroscopic data (PDF)

AUTHOR INFORMATION

Corresponding Authors

*Mohamed.Qenawy@kemi.uu.se
Leif.Hammarstrom@kemi.uu.se

ORCID

Erwin Reisner: 0000-0002-7781-1616
Leif Hammarström: 0000-0002-9933-9084

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors are grateful for funding from the Knut and Alice Wallenberg Foundation, the Swedish Energy Agency, the Swedish Research Council, the Austrian Christian Doppler Research Association (Austrian Federal Ministry of Science, Research and Economy and the National Foundation for Research, Technology and Development), and the OMV Group. Dr. Mohammad Mirmohades, Jens Föhlinger, and Luca D’Amario are acknowledged for their help with fs-TRIR and ns-FTIR. Prof. Sascha Ott is also acknowledged for his helpful discussion. We are dedicating this work to the soul of Prof. Ahmed Zewail.

REFERENCES