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J. Am. Chem. Soc., Just Accepted Manuscript • DOI: 10.1021/jacs.9b12443 • Publication Date (Web): 04 Mar 2020 Downloaded from pubs.acs.org on March 4, 2020

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Tracking Mechanistic Pathway of Photocatalytic CO₂ Reaction at Ni Sites Using Operando, Time-Resolved Spectroscopy

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KEYWORDS. Time-resolved spectroscopy; Operando spectroscopy; Photocatalysis; Mechanistic pathway; CO₂ Reduction.

Supporting Information Placeholder

ABSTRACT: Harvesting solar energy for catalytic conversion of CO_2 into valuable chemical fuels/feedstocks is an attractive yet challenging strategy to realize a sustainable carbon-cycle utilization. Homogeneous catalysts typically exhibit higher activity and selectivity as compared with heterogeneous counterparts, benefiting from their atomically dispersed catalytic sites and versatile coordination structures. However, it is still a "black box" how the coordination and electronic structures of catalysts dynamically evolve during the reaction, forming the bottleneck for understanding their reaction pathways. Herein, we demonstrate to track the mechanistic pathway of photocatalytic CO_2 reduction using terpyridine nickel(II) complex as a catalyst model. Integrated with a typical homogeneous photosensitizer, the catalytic system offers a high selectivity of 99% for CO_2 -to-CO conversion with turnover number and turnover frequency as high as 2.36×10^7 and 385.6 s^{-1} , respectively. We employ operando and time-resolved X-ray absorption spectroscopy, in combination with other in situ spectroscopic techniques and theoretical computation, to track the intermediate species of Ni catalyst in the photocatalytic CO_2 reduction reaction for the first time. Taken together with the charge dynamics resolved by optical transient absorption spectroscopy, the investigation elucidates the full mechanistic reaction pathway including some key factors that have been often overlooked. This work opens the "black box" for CO_2 reduction in the system of homogeneous catalysts, and provides key information for developing efficient catalysts towards artificial photosynthesis.

INTRODUCTION

Increasing concerns about energy crisis and excessive CO_2 emission have urged scientists to exploit new clean energy to address the irreplaceable demand for fossil fuels. The solardriven reduction of CO_2 into chemical fuels/feedstocks is a promising strategy to address the issues while highly efficient and selective reduction of CO_2 still remains a grand challenge owing to the large bond energy of CO_2 and the diversity of CO_2 reduction products.¹⁻³ In the past few decades, great research efforts have been devoted to exploring efficient catalysts for photocatalytic CO_2 reduction, striving to achieve artificial photosynthesis.⁴⁻⁷

Typically, homogeneous catalysts exhibit high activity and selectivity towards artificial photosynthesis compared with heterogeneous counterparts.⁸ The homogeneous catalysts are commonly referred to as metal complexes, in which metal ions are coordinated by organic ligands. Altering the ligands

coordinated to the metal center, the redox potential and electronic structure of the catalyst can be readily modulated to tune catalytic activity and selectivity. Moreover, the atomically dispersed active sites in homogeneous catalysts are better chemically defined, facilitating the determination of reaction mechanisms.⁸ These advantages designate the homogeneous system an ideal model to explore the reaction mechanisms of photocatalytic CO₂ reduction, which would provide valuable information for rationally designing heterogeneous catalysts. However, the dynamic evolution of coordination and electronic structures for homogeneous catalysts during photocatalytic CO₂ reduction closely associated with reaction pathways are still a "black box". Such a black box is rather complex than common assumption in the sense that even the non-protonic solvent used for homogeneous catalysts, typically CH₃CN, may participate in the reaction pathways and impact on the catalytic performance of CO₂ reduction. To gain key information on how homogeneous catalysts work efficiently during the reaction, it is imperative to track the mechanistic pathways using operando, time-resolved and element-specific spectroscopic techniques.



Scheme 1. The photocatalytic system consisting of $[Ni(tpy)_2]^{2+}$ catalyst, $[Ru(bpy)_3]^{2+}$ photosensitizer, and BIH electron donor.

Herein, we demonstrate the elucidation of reaction pathways using time-resolved X-ray absorption spectroscopy (TR-XAS) in combination with other spectroscopic techniques and theoretical computation. As a proof of concept, we employ $[Ni(tpy)_2]^{2+}$ (tpy = 2.2':6'.2"-terpyridine) complex as a homogeneous catalysts model to open the "black box" in photocatalytic CO₂ reduction. Polypyridyl transition metal complexes are one class of the most extensively studied homogeneous catalysts for CO₂ reduction, benefiting from the redox active nature of polypyridine backbone. The reduced polypyridyl rings can act as the reservoir of photo-induced electrons, and in turn, the metal center mediates the transfer of the electrons to CO₂ molecules.⁹⁻¹¹ Using the model catalyst of [Ni(tpy)₂]²⁺ complex, we achieve highly efficient and selective reduction of CO₂ to CO in a photocatalytic system with $[Ru(bpy)_3]^{2+}$ (bpy = 2,2'-bipyridine) as a photosensitizer and 1,3-dimethyl-2-phenyl-2,3-dihydro-1Hbenzo[d]imidazole (BIH) as an electron donor (Scheme 1). The high activity and selectivity for CO₂ reduction urge us to track the intermediate species of $[Ni(tpy)_2]^{2+}$ catalyst during the reaction in terms of dynamic coordination and electronic structures by employing the TR-XAS and other in situ spectroscopic techniques. In combination with charge dynamics information, this research can elucidate the full mechanistic pathway involving the

EXPERIMENTAL SECTION

catalyst, photosensitizer, electron donor and solvent.

Time-resolved X-ray absorption spectroscopy (TR-XAS). The TR-XAS measurements (the setup as shown in Figure S1) were performed at the beamline 1W2B in the Beijing Synchrotron Radiation Facility (BSRF), China, and the detail of the setup has been described in a previous report.¹² The high repetition rate and ultra-short pulse fiber laser (Tangerine HP, Amplitude systems) was utilized to excite sample. The laser spot size is $150 \times 160 \ \mu\text{m}$. Laser repetition rate was set to 75 kHz with a power of 1.5 W to sufficiently excite the sample. The sample was circulated by a peristaltic pump to avoid radiation damage and showed no degradation after X-ray and laser illumination. The sample chamber provided an air-tight environment with CO₂ gas purging during the measurement. The K-edge spectra of the terpyridine nickel (II) complex were collected by fluorescence mode using homemade avalanche photodiode detectors (APDs).

In situ diffuse reflectance infrared Fourier-transform spectroscopy (DRIFTS). In situ DRIFTS measurements were performed using a Bruker IFS 66v Fourier transform spectrometer equipped with a Harrick diffuse reflectance accessory at the Infrared Spectroscopy and Microspectroscopy Endstation (BL01B) in the National Synchrotron Radiation Laboratory (NSRL) in Hefei, China. Each spectrum was recorded by averaging 128 scans at a resolution of 2 cm⁻¹. The samples were mixed with KBr by a mortar and were held in a custom-fabricated IR reaction chamber which was specifically designed to examine highly scattered powder samples in diffuse reflection mode. The chamber was sealed with two ZnSe windows. Pure KBr powder was first measured to obtain a background spectrum. During the in situ characterization, pure CO_2 (99.999%) or N₂ (99.999%) saturated by CH_3CN/H_2O vapor was continually introduced into the chamber. The spectra were collected under dark condition or after a certain irradiation time using a 5 W UV LED (UVEC-4II). The spectra were obtained by subtracting the background from the spectra of samples.

Operando surface-enhanced Raman spectroscopy (SERS). Operando SERS spectra were recorded using a WITec alpha 300R confocal Raman microscope with a 600 grooves/mm diffraction grating. As the excitation source, a 633 nm solid-state laser with an exact power of 20 mW was used with attenuation by a filter. Calibration was performed using a silicon wafer standard (520 cm⁻¹). A CCD with 1650 × 200 pixels was used to collect the spectra. The CO₂-saturated sample solution and indium tin oxide (ITO, 2×10 mm) plated with 50 nm Au nanocubes were sealed in the quartz cuvette ($3 \times 1 \times 1$ cm). During the in situ characterization, the spectra were collected continuously under UV irradiation using a 5 W UV LED (UVEC-4II).

Time-resolved optical transient absorption (OTA) The nanosecond-to-microsecond transient spectroscopy. spectroscopy measurements were performed using a commercial nanosecond laser flash photolysis spectrometer (LP980-KS, Edinburgh Instruments Ltd, Livingston, UK) at room temperature. A pulsed Nd: YAG laser (Quanta-Ray LAB190, Spectra-Physics) with an optical parametric oscillator (PrimoScan ULD400, Spectra-Physics) for wavelength conversion was used for excitation, and the probing light was generated by a 150 W pulsed xenon arc-lamp at a repetition of 1 Hz and perpendicular to the pump light. Typical experiments employed laser excitation at 440 nm (10 mJ/pulse, 3-6 ns fwhm). The single-wavelength transient absorption was monitored at the indicated wavelengths (0.3-2.0 nm band widths) with a photomultiplier tube (PMT) detector (Hamamatsu R928), which was connected to a Tektronix Model MDO3052 (100 MHz 1.25 GS/s) digital oscilloscope. The transient spectra were recorded using an ICCD camera (DH320T, Andor) at chosen indicated time delays. For all records, the probe background was collected between two laser shots and subtracted from the signal, and emission background was subtracted where relevant. Transient absorption spectra and kinetics were acquired using the L900 software (Edinburgh Instruments) and processed using Origin 8.5 software. A quartz cell cuvette with a 1×1 cm was used for measurements, and the samples were bubbled with Ar before measurement.

Theoretical calculations. The hybrid functional B3LYP was used for electronic structure calculations as implemented in Gaussian 09 program. Geometry optimization was performed with 6-31G(d) basis sets on all elements. The solvation energy in the mixture of water and acetonitrile was calculated using the SMD continuum solvation model. D3 dispersion correction, proposed by Grimme, was also added. Analytic frequency calculations were carried out on all optimized structures at the

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same level of theory, to identify all stationary points as minima (no imaginary frequency) and to obtain zero-point energy corrections.

RESULTS AND DISCUSSION

The [Ni(tpy)₂]²⁺ (namely, Ni(II)) catalyst and BIH electron donor are synthesized by following the protocols in SI and then characterized by high-resolution mass spectroscopy (HRMS, Figure S2), elemental analysis and UV-vis absorption spectroscopy (Figure S3). We first evaluate the performance of photocatalytic CO₂ reduction in a quartz reactor containing Ni(II) catalyst, [Ru(bpy)₃]²⁺ (namely, Ru(II)) photosensitizer and BIH electron donor in CH3CN/H2O solvent. After optimizing the reaction conditions, the Ni(II) catalyst exhibits a high turnover number (TON) of 2.36×107 and turnover frequency (TOF) of 385.6 s⁻¹ with a CO selectivity up to 99% (Figure S4), two orders of magnitude higher than the TON and TOF records as ever reported in the state-of-the-art homogeneous catalysts for photocatalytic CO₂ reduction (Table S1). The isotope-labeled ${}^{13}CO_2$ experiments confirm that the produced CO indeed originates from the CO₂ reduction (Figure S5). In addition to activity and selectivity, the Ni(II) catalyst can undergo a complete catalytic cycle and maintain its valence state after the reaction, offering excellent stability (Figure S6-S8). The durability test shows a stagnation for the yield of CO upon irradiation for 21 h only caused by the degradation of Ru(II) photosensitizer, while the supplement of Ru(II) can reactivate such nearly ceased photocatalytic CO2-to-CO conversion.

Given that the Ni(II) complex has achieved high catalytic activity and selectivity, we are now in a position to explore the long-standing "black box" how exactly the homogeneous catalysts work efficiently for the reaction. Such a puzzle refers to the dynamic coordination and electronic structures of the Ni(II) complex during the reaction, the role of the solvent on catalytic performance, and the key steps for determining product selectivity and conversion efficiency, constituting the full mechanistic pathway. To decode the puzzle, we employ operando TR-XAS to track the intermediate species of Ni(II) complex during the photocatalytic CO₂ reduction process. As a powerful element-specific tool, TR-XAS has been applied to resolve the information for the local coordination and electronic structures of transient species in the system of homogeneous hydrogen production with metal complexes.¹³⁻¹⁶ Nevertheless, such a technique has not been employed to examine photocatalytic CO₂ reduction – a substantially more complicated system than hydrogen production. This complicated system involves both CO₂ and organic solvent so that tracking the local coordination and electronic structures of the catalyst exposed to the CO_2 and solvent molecules is crucial to the deep understanding of reaction mechanism. To track the intermediates of Ni(II) complex during the photocatalytic CO₂ reduction reaction, operando Ni K-edge X-ray absorption nearedge structure (XANES) spectra are collected for the Ni(II) complex before (laser-off) and after (laser-on) laser excitation. The multiple scattering calculation is performed using FEFF9 software on a cluster with radius of 6.5 Å.¹⁷ Figure 1a shows the Ni K-edge XANES spectra. The ground-state fitting XANES spectrum indicates that the optimized ground-state geometry structure of the Ni(II) complex is a six-coordinated Ni-N₆ octahedral configuration as shown in Figure 1b. In the structure, the predominant strain component of the rigid terpyridine ligand corresponds to a distinct compression along the molecular z axis of the NiN₆ octahedron. The ${}^{3}A_{2g}$ ground state of octahedral Ni(II) is *Jahn-Teller* stable while the NiN₆ geometry solely reflects the strain effects imposed by the ligands and/or steric packing effects in the unit cell (refer to the Ni-N bond lengths, Table S2 and S3).¹⁸



Figure 1. The Ni transient X-ray absorption spectra obtained in a system consisting of 1 mM Ni(II) catalyst, 1.5 mM Ru(II), and 10 mM BIH by 345 nm laser excitation in degassed CH₃CN/H₂O solution: (a) Experimental XANES spectrum of Ni(II) complex at ground state (black), the ground-state fitting XANES spectrum based on the structure in Panel b, and the reconstructed transient fitting spectrum based on the structure in Panel d. (b) The optimized structure of ground-state Ni(II) complex. (c) Transient XANES spectrum (red) at 0.4 µs after laser excitation and ground-state spectrum (black dotted line). The difference spectra from three TR-XAS scans (hollow circles) were obtained by subtracting the ground-state spectrum from the transient one, respectively. The corresponding XANES difference fitting spectrum (blue) was presented with the fitted intermediate fraction 4.2%. (d) The optimized structure of Ni intermediate. N1 is located at the benzene ring in the middle of the terpyridine ligand, and N2 is located at the benzene ring in the two sides of the terpyridine ligand.

Upon light excitation, transient intermediate species is formed within 0.4 µs. As the experimental transient spectrum contains the signals from both the ground state and transient state, the difference spectrum is obtained to highlight the intermediate state by subtracting the ground signal from the transient spectrum. Figure 1c shows the difference spectra from three TR-XAS scans obtained for the given pump-probe delay time (the corresponding XANES data are shown in Figure S9), which provides the information on the local atomic structure around the Ni atom and its oxidation state. The change in the Ni coordination environment can be indicated by the combination of XANES fitting with first-principles calculation. XANES fitting reveals that the optimized intermediate structure possesses a penta-coordinated distorted tetrahedron configuration as shown in Figure 1d (the corresponding difference XANES fitting procedure is shown in Figure S10). Such penta-coordinated structure acquired from XANES fitting

a 0.8

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0 2

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-0.4

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Abs (510nm) 2010 2010

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-200

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is consistent with the intermediate obtained from density function theory (DFT)-calculated free energy profiles, which will be discussed in the following section. This indicates that after photoexcitation, one terpyridine ligand is detached from the Ni(II) complex when the central Ni ion is combined with CO₂ and CH₃CN, resulting in a non-central geometric symmetry. In such an intermediate structure, the Ni-N (Ni-N2) bond on both sides of the terpyridine ligand is shortened while the middle Ni-N (Ni-N1) bond is elongated (Table S2). The positive feature at 8344 eV (peak A) originating from the absorption edge shifts to lower energy, and the negative dip at 8354 eV (peak B) corresponding to the white-line peak for the Ni intermediate is lower than that of the ground-state Ni(II) complex. This observation indicates the formation of reduced Ni(I) intermediate, induced by the transfer of photogenerated electrons from the photosensitizer to Ni(II) complex. The percentage of the Ni(I) intermediate obtained after laser excitation is determined to about 4.2% by the XANES fitting. The reconstructed transient fitting spectrum based on the structure in Panel d is also shown in Figure 1a, convincing the claim about the reduction of Ni(II) to Ni(I).

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Figure 2. (a) In situ DRIFTS spectra collected in N₂ or CO₂ atmosphere under irradiation in a reaction system containing Ru(II), BIH and Ni(II) in CH₃CN/H₂O vapor. The system is irradiated with a 365 nm LED lamp. (b) Operando SERS spectra collected during photocatalytic CO₂ reduction in a reaction system containing Ru(II), BIH and Ni(II) in CH₃CN/H₂O solvent. The system is irradiated with a 365 nm LED lamp, and 50 nm Au nanocubes are used as SERS substrates.

To gain more information for chemical bonding, we further employ in situ diffuse reflectance infrared Fourier-transform spectroscopy (DRIFTS) and operando surface-enhanced Raman spectroscopy (SERS) to detect the potential intermediate species during the reaction process, in which the background is subtracted to exclude environment factors as well as the signals from Ni(II) complex and free molecular CO₂. In the in situ DRIFTS spectra, no additional vibration peaks can be observed during irradiation up to 60 min in N₂ atmosphere (Figure 2a) or under dark condition (Figure S11). In comparison, two bands at 1662 and 1622 cm-1 appear significantly after irradiation for 5 min in CO₂ atmosphere, attributed to the formation of a Ni-CO2⁻ or Ni-CO2H complex.^{19,20} Moreover, complementary information for intermediate species is provided by operando SERS measurement. As shown in Figure 2b, no peaks are present for CO₂-saturated CH₃CN/H₂O solvent before irradiation. Upon irradiation, three peaks are observed at 1604, 1553, and 1485 cm⁻¹ that can be assigned to carboxylate COO-, while another peak around 2040 cm⁻¹ is attributed to C=O stretching vibration.²¹⁻²³ These results from in situ DRIFT and operando SERS further confirm the existence of intermediate species tracked by TR-XAS.



Figure 3. Optical transient absorption spectra of different systems following 440 nm laser excitation (1 Hz, ~10 mJ/pulse) in degassed mixed solution: (a) Spectra of 0.15 mM Ru(II) after laser excitation for 0-4 µs. (b) Spectra of 0.15 mM Ru(II) and 0.1 mM Ni(II) after laser excitation for 0-4 µs. (c) Spectra of 0.15 mM Ru(II) and 1 mM BIH after laser excitation for 0-200 $\mu s.~$ (d) Spectra of 0.15 mM Ru(II), 0.1 mM Ni(II) and 1 mM BIH after laser excitation for 0-200 µs. (e) Kinetic analysis of the Ru(I) signal growth probed at 510 nm in the absence (red trace) and presence (blue trace) of 0.1 mM Ni(II) catalyst. (f) Kinetic analysis of the Ru(I) signal decay probed at 510 nm in the absence (red trace) and presence (blue trace) of 0.1 mM Ni(II) catalyst.

0.00

-0.05

20

Time (µs)

30

- = 198 ns

Ni(II) T. = 172 ns

800 1000

600

Ru(II) -BIH

400

Time (ns)

The information gleaned above has revealed the formation of reduced Ni(I) intermediate which should be induced by the transfer of photogenerated electrons from Ru(II) photosensitizers to Ni(II) complex. Then a question naturally arises how the photogenerated electrons behave during the reaction. To investigate the dynamics of photogenerated electrons involved in the system, electrochemical measurement is first performed to examine the redox potentials of the components - BIH and Ni(II) complex (Figure S12). As indicated by the redox potentials (Figure S13), the transfer of electrons from the photo-induced excited *Ru(II) photosensitizer $(-0.81 \text{ V})^{24}$ to the Ni(II) catalyst (-1.27 V) is thermodynamically unfavorable. As such, essentially the catalytic process should occur through a reduction quenching pathway. The excited *Ru(II) is quenched by BIH to form Ru(I) which in turn delivers one electron to the Ni(II) catalyst to yield a reduced Ni(I) intermediate for CO₂ reduction, simultaneously regenerating Ru(II). To further prove the dynamic process, we collect photoluminescence (PL) spectra and analyze



Figure 4. (a) The free energy profiles for CO_2 reduction by $[Ni(tpy)]^0$ in both low-spin and high-spin states (ACN: acetonitrile) calculated by DFT. (b) Schematic mechanistic pathway for the CO_2 reduction reaction catalyzed by $[Ni(tpy)]^0$.

luminescence lifetime. It turns out that BIH can quench the luminescence of Ru(II) photosensitizer while Ni(II) cannot (Figure S14), indicating that photogenerated electrons are not directly transferred from the Ru(II) photosensitizer to the Ni(II) catalyst. In the presence of BIH, however, the addition of Ni(II) catalyst can further quench the luminescence of Ru(II) photosensitizer. This phenomenon can be ascribed to the mechanism that the formed Ru(I) delivers one electron to the Ni(II) catalyst by regenerating Ru(II), shifting the quenching equilibrium of excited *Ru(II) to Ru(I). This argument is also supported by the luminescence lifetime comparison as shown in Figure S15. The luminescence lifetime of Ru(II) decays from 256.9 ns to 170.6 ns with the addition of BIH while the sole presence of Ni(II) catalyst does not significantly alter the lifetime (245.4 ns). In the presence of BIH, the luminescence lifetime of Ru(II) further decays from 170.6 ns to 127.6 ns by shifting the quenching equilibrium of excited *Ru(II) to Ru(I) with the addition of Ni(II) catalyst, further confirming the efficient electron transfer from Ru(I) to Ni(II).

To elucidate the electron dynamics, optical transient absorption (OTA) spectroscopy is further employed to examine the photocatalytic system (Figure 3, S15-S18). As shown in Figure 3a-d, upon laser excitation of the system at 440 nm, the bleaching signal of ground-state Ru(II) and the absorption attenuation signal of excited-state *Ru(II) appear at 446 nm and 365 nm, respectively. With the addition of BIH, an additional absorption band located at 510 nm can be observed (Figure 3c, d). This suggests the formation of Ru(I) by quenching excitedstate *Ru(II) with BIH, consistent with the findings from PL spectra and lifetime characterizations (Figure S14 and S15). Furthermore, the addition of Ni(II) catalyst does not alter the kinetics of forming Ru(I) but remarkably facilitates the decay of Ru(I) species. As shown in Figure 3e, there is no significant difference for the signal growth of Ru(I) in the presence and

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absence of Ni(II) (172 ns vs. 198 ns). However, the signal decay of Ru(I) is accelerated significantly by the addition of Ni(II) with a rate constant of 1.36×10^9 M⁻¹ s⁻¹ (Figure 3f, 7.89 µs without Ni(II) vs. 3.8 µs with Ni(II)). Such a twice faster decay is a solid indicator of efficient electron transfer from Ru(I) to Ni(II) through BIH, manifesting the reduction quenching mechanism of the Ru(II)/Ni(II)/BIH photocatalytic system.

Based on the information on the coordination and electronic structures of intermediate species, we further depict the free energy profiles of CO₂-to-CO reduction reaction catalyzed by [Ni(tpy)]²⁺ by DFT calculations. Since [Ni(tpy)₂]²⁺ can accept one electron by divalent Ni metal ions to form [Ni(tpy)2]+ and further accept one electron by a terpyridine ligand to form $[Ni(tpy)_2]^0$ before initiating the CO₂ reduction reaction (CO₂RR),²⁵ we compare the formation energies of [Ni(tpy)]⁺ (35.45 kcal/mol for low spin and 49.43 kcal/mol for high spin, Figure S20) and [Ni(tpy)]⁰ (17.80 kcal/mol for low spin and 32.06 kcal/mol for high spin, Figure 4a). The comparison reveals that the latter requires less energy input in the following step of detaching a terpyridine ligand. In this case, we mainly present the reaction profiles associated with [Ni(tpy)]⁰ here. In addition, the calculations show that the simultaneous coordination of acetonitrile and CO₂ to the Ni center is stronger than that of H2O and CO2 by 2.4 kcal/mol in binding energy (see supporting information for details, Table S4), suggesting that the Ni center prefers to simultaneously coordinate with acetonitrile and CO₂. Furthermore, owing to stereo repulsion, H₂O could not bind to Ni center when coordinated with acetonitrile and CO₂. Meanwhile, although H₂O may provide protons to facilitate the CO₂ reduction to CO through the dihydroxyl pathway in aqueous environment, both the selectivity and yield of CO production decrease with the increase of water content due to the competitive hydrogen evolution (Figure S4c), indicating that H₂O would hinder the CO₂ reduction. Taken together, the calculation results can reach the conclusion that the acetonitrile and CO₂ rather than H₂O and other ligands are simultaneously coordinated to the Ni center. This conclusion is consistent with the result from the difference XANES fitting for TR-XAS spectra, which suggests that the intermediate is a five-coordinated Ni species with the most likely structure Ni(tpy)(CO₂)(CH₃CN) as depicted in Figure 1d. DFT calculation shows that the attached CO₂ is bent with a \angle OCO of 144.96° at low spin and 140.68° at high spin, respectively. As revealed by Mulliken population analysis, the low-spin and high-spin states carry a negative charge of 0.38 eand 0.49 e⁻, respectively. This clearly indicates the formation of anionic O=C-O- in the intermediate complex, which is generally assumed as the rate-limiting step of CO₂RR.²¹ As the reduction reaction proceeds to generate CO, it can go either the dihydroxyl pathway involving protons in aqueous environment or the carbonate pathway involving a second CO₂ in nonaqueous environment.^{20, 26} By adopting the Zundel $(H_5O_2^+)$ as the form of hydronium in our calculation,^{27,28} we reveal that the dihydroxyl pathway is more favorable than the carbonate pathway in both low spin (-21.33 kcal/mol vs. -17.39 kcal/mol) and high spin (-12.55 kcal/mol vs. -6.80 kcal/mol) states, regarding to their respective free energy changes. As a result, we conclude that CO₂RR in our catalytic system should undergo the dehydroxyl pathway.

Taken together, the coordination structure, electronic structure, charge dynamics and reaction free energy provide the essential information for proposing the full reaction pathway. As illustrated in Figure 4b, $[Ni^{II}(tpy)_2]^{2+}$ (a) accepts two

photogenerated electrons to form [Ni^I(tpy)(tpy)⁻]⁰ (b) that subsequently loses a neutral terpyridine ligand, leaving a coordinatively unsaturated and catalytically active Ni species (c). As a result, the vacant site on the catalytically active Ni species can be combined with CO2 and solvent CH3CN molecules, generating а five-coordinated Ni(tpy)(CO₂)(CH₃CN) species (d). The next step is protonation of the anionic $O=C-O^{-1}$ in the intermediate complex to form the intermediate adduct (e). Following closely, CO formation requires an extra electron so as to trigger C–O bond cleavage, and complexes (f) and (g) are formed successively via a coupled electron-proton transfer-bond breaking step.29 Eventually, CO and solvent CH₃CN molecules are released to complete the cvcle.

CONCLUSION

In conclusion, we have successfully identified the dynamic coordination and electronic structures of a Ni complex catalyst in a homogeneous photocatalytic system for CO₂ reduction by operando TR-XAS spectroscopy. It has revealed that the reduced Ni(I) intermediate is coordinated with a terpyridine ligand, CO₂ and solvent CH₃CN molecules to generate a fivecoordinated Ni(tpy)(CO₂)(CH₃CN) species. Such an intermediate specie has also been confirmed by in situ DRIFTS and operando SERS. The formation of reduced Ni(I) intermediate is induced by the transfer of photogenerated electrons from photosensitizer to terpyridine nickel(II) complex whose dynamics has been resolved by OTA spectroscopy. Combined with the detail DFT calculation, the experimental evidence based on operando and time-resolved spectroscopy provides a direct view for the full mechanistic pathway. The findings in this work represent a step forward in opening the "black box" of CO₂ reduction in highly efficient homogeneous photocatalytic systems. For instance, this work highlights the key role of solvent molecules in reactions, which has been often overlooked, and elucidates how homogeneous photosensitizer, catalyst and electron donor work synergistically for photocatalytic CO₂ reduction. This work also provides insights rationally designing and developing advanced for photocatalytic systems for artificial photosynthesis from the angle of catalytic sites.

ASSOCIATED CONTENT

Supporting Information

Detailed experimental section, characterization methods, and additional material characterizations. The Supporting Information is available free of charge on the ACS Publications website.

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The manuscript was written through contributions of all authors. **Notes**

The authors declare no competing financial interests.

ACKNOWLEDGMENT

This work was supported by National Key R&D Program of China (2017YFA0207301), NSFC (21725102, 91961106, 21703220,

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U1332205, 21773012 and 91753118), CAS Key Research Program of Frontier Sciences (QYZDB-SSW-SLH018), DNL Cooperation Fund, CAS (DNL201922), Beijing Natural Science Foundation (L172028) and CAS Interdisciplinary Innovation Team. TR-XAS characterization was performed at the beamline 1W2B in the Beijing Synchrotron Radiation Facility (BSRF), China. In situ DRIFTS was collected at the Infrared Spectroscopy and Microspectroscopy Endstation (BL01B) in the National Synchrotron Radiation Laboratory (NSRL) in Hefei, China.

REFERENCES

- 11
 12
 (1) Kuriki, R.; Sekizawa, K.; Ishitani, O.; Maeda, K. Visible-light-driven CO₂ reduction with carbon nitride: enhancing the activity of ruthenium catalysts. *Angew. Chem. Int. Ed.* 2015, *54*, 2406.
- (2) Rao, H.; Schmidt, L. C.; Bonin, J.; Robert, M. Visible-light-driven
 methane formation from CO₂ with a molecular iron catalyst. *Nature*2017, 548, 74.
- (3) Guo, Z.; Chen, G.; Cometto, C.; Ma, B.; Zhao, H.; Groizard, T.; Chen, L.; Fan, H.; Man, W. L.; Yiu, S. M.; Lau, K. C.; Lau, T. C.;
- 18Robert, M. Selectivity control of CO versus $HCOO^-$ production in the19visible-light-driven catalytic reduction of CO_2 with two cooperative20metal sites. Nat. Catal. 2019, 2, 801.
- (4) Cui, X.; Wang, J.; Liu, B.; Ling, S.; Long, R.; Xiong, Y. Turning Au nanoclusters catalytically active for visible-light-driven CO₂ reduction through bridging ligands. J. Am. Chem. Soc. 2018, 140, 16514.
- (5) Wang, J.; Xia, T.; Wang, L.; Zheng, X.; Qi, Z.; Gao, C.; Zhu, J.; Li, Z.; Xu, H.; Xiong, Y. Enabling visible-light-driven selective CO₂ reduction by doping quantum dots: trapping electrons and suppressing H₂ evolution. *Angew. Chem. Int. Ed.* 2018, *57*, 16447.
- (6) Choi, K. M.; Kim, D.; Rungtaweevoranit, B.; Trickett, C. A.;
 Barmanbek, J. T. D.; Alshammari, A. S.; Yang, P.; Yaghi, O. M.
 Plasmon-enhanced photocatalytic CO₂ conversion within metalorganic frameworks under visible light. J. Am. Chem. Soc. 2017, 139, 356.
- (7) Gao, C.; Chen, S.; Wang, Y.; Wang, J.; Zheng, X.; Zhu, J.; Song,
 L.; Zhang, W.; Xiong, Y. Heterogeneous single-atom catalyst for
 visible-light-driven high-turnover CO₂ reduction: the role of electron
 transfer. Adv. Mater. 2018, 30, 1704624.
- (8) Gao, C.; Wang, J.; Xu, H.; Xiong, Y. Coordination chemistry in the design of heterogeneous photocatalysts. *Chem. Soc. Rev.* 2017, 46, 2799.
- (9) Elgrishi, N.; Chambers, M. B.; Wang, X.; Fontecave, M. Molecular
 polypyridine-based metal complexes as catalysts for the reduction of CO₂. *Chem. Soc. Rev.* 2017, *46*, 761.
- (10) Wang, J. W.; Liu, W. J.; Zhong, D. C.; Lu, T. B. Nickel complexes as molecular catalysts for water splitting and CO₂ reduction. *Coordin. Chem. Rev.* 2019, *378*, 237.
- 42 (11) Elgrishi, N.; Chambers, M. B.; Artero, V.; Fontecave, M. Terpyridine complexes of first row transition metals and electrochemical reduction of CO₂ to CO. *Phys. Chem. Chem. Phys.*44 2014, 16, 13635.
- (12) Wang, H.; Yu, C.; Wei, X.; Gao, Z.; Xu, G. L.; Sun, D. R.; Li, Z.;
 Zhou, Y.; Li, Q. J.; Zhang, B. B.; Xu, J. Q.; Wang, L.; Zhang, Y.; Tan,
 Y. L.; Tao, Y. Development of picosecond time-resolved X-ray absorption spectroscopy by high-repetition-rate laser pump/X-ray probe at Beijing Synchrotron Radiation Facility. *J. Synchrotron. Radiat*2017, 24, 667.
- 50 (13) Moonshiram, D.; Guda, A.; Kohler, L.; Picon, A.; Guda, S.;
 51 Lehmann, C. S.; Zhang, X.; Southworth, S. H.; Mulfort, K. L. Mechanistic evaluation of a nickel proton reduction catalyst using time-

resolved X-ray absorption spectroscopy. J. Phys. Chem. C 2016, 120, 20049.

(14) Moonshiram, D.; Gimbert-Suriñach, C.; Guda, A.; Picon, A.; Lehmann, C. S.; Zhang, X.; Doumy, G.; March, A. M.; Benet-Buchholz, J.; Soldatov, A.; Llobet, A.; Southworth, S. H. Tracking the structural and electronic configurations of a cobalt proton reduction catalyst in water. *J. Am. Chem. Soc.* **2016**, *138*, 10586.

(15) Li, Z. J.; Zhan, F.; Xiao, H.; Zhang, X.; Kong, Q. Y.; Fan, X. B.; Liu, W. Q.; Huang, M. Y.; Huang, C.; Gao, Y. J.; Li, X. B.; Meng, Q. Y.; Feng, K.; Chen, B.; Tung, C. H.; Zhao, H. F.; Tao, Y.; Wu, L. Z. Tracking Co(I) intermediate in operando in photocatalytic hydrogen evolution by X-ray transient absorption spectroscopy and DFT calculation. J. Phys. Chem. Lett. **2016**, 7, 5253.

(16) Smolentsev, G.; Soldatov, M. A.; Probst, B.; Bachmann, C.; Azzaroli, N.; Alberto, R.; Nachtegaal, M.; van Bokhoven, J. A. Structure of the Co¹ intermediate of a Cobalt pentapyridyl catalyst for hydrogen evolution revealed by time-resolved X-ray spectroscopy. *ChemSusChem* **2018**, *11*, 3087.

(17) Rehr, J. J.; Kas, J. J.; Vila, F. D.; Prange, M. P.; Jorissen, K. Parameter-free calculations of X-ray spectra with FEFF9. *Phys. Chem. Chem. Phys.* **2010**, *12*, 5503.

(18) Folgado, J. V.; Henke, W.; Allmann, R.; Stratemeier, H.; Beltran-Porter, D.; Rojo, T.; Reinen, D. Fluxionality in hexacoordinated copper (II) complexes with 2, 2': 6', 2"-terpyridine (Terpy) and related ligands: structural and spectroscopic investigations. *Inorg. Chem.* **1990**, *29*, 2035.

(19) Sampson, M. D.; Froehlich, J. D.; Smieja, J. M.; Benson, E. E.; Sharp, I. D.; Kubiak, C. P. Direct observation of the reduction of carbon dioxide by rhenium bipyridine catalysts. *Energy Environ. Sci.* **2013**, *6*, 3748.

(20) Kuehnel, M. F.; Orchard, K. L.; Dalle, K. E.; Reisner, E. Selective photocatalytic CO₂ reduction in water through anchoring of a molecular Ni catalyst on CdS nanocrystals. *J. Am. Chem. Soc.* **2017**, *139*, 7217.

(21) Chernyshova, I. V.; Somasundaran, P.; Ponnurangam, S. On the origin of the elusive first intermediate of CO₂ electroreduction. *Proc. Natl. Acad. Sci. U.S.A.* **2018**, *115*, E9261.

(22) Jiang, S.; Klingan, K.; Pasquini, C.; Dau, H. New aspects of operando Raman spectroscopy applied to electrochemical CO₂ reduction on Cu foams. *J. Chem. Phys.* **2019**, *150*, 041718.

(23) Tammer, M. G. Sokrates: Infrared and Raman characteristic group frequencies: tables and charts. *Colloid Polym. Sci.* **2004**, *283*, 235.

(24) Prier, C. K.; Rankic, D. A.; MacMillan, D. W. C. Visible light photoredox catalysis with transition metal complexes: applications in organic synthesis. *Chem. Rev.* **2013**, *113*, 5322.

(25) Wang, M.; England, J.; Weyhermüller, T.; Wieghardt, K. Electronic structures of "low-valent" neutral complexes $[NiL_2]^0$ (S = 0; L = bpy, phen, tpy) – an experimental and DFT computational study. *Eur. J. Inorg. Chem.* **2015**, *2015*, 1511.

(26) Barlow, J. M.; Yang, J. Y. Thermodynamic considerations for optimizing selective CO_2 reduction by molecular catalysts. *ACS Cent. Sci.* **2019**, *5*, 580.

(27) Dahms, F.; Costard, R.; Pines, E.; Fingerhut, B. P.; Nibbering, E. T. J.; Elsaesser, T. The hydrated excess proton in the Zundel cation $H_5O_2^+$: the role of ultrafast solvent fluctuations. *Angew. Chem. Int. Ed.* **2016**, *55*, 10600.

(28) Park, M.; Shin, I.; Singh, N. J.; Kim, K. S. Eigen and Zundel forms of small protonated water clusters: structures and infrared spectra. *J. Phys. Chem. A* **2007**, *111*, 10692.

(29) Bonin, J.; Maurin, A.; Robert, M. Molecular catalysis of the electrochemical and photochemical reduction of CO₂ with Fe and Co metal based complexes. Recent advances. *Coordin. Chem. Rev.* **2017**, *334*, 184.

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