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CO₂ reduction with Re(ı)–NHC compounds: driving selective catalysis with a silicon nanowire photoelectrode[†]

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The CO₂-reduction activity of two Re(i)–NHC complexes is investigated employing a silicon nanowire photoelectrode to drive catalysis. Photovoltages greater than 440 mV are observed along with excellent selectivity towards CO over H₂ formation. The observed selectivity towards CO production correlates with strong adsorption of the catalysts on the photoelectrode surface.

Many transition metal complexes have exhibited catalytic activity for multi-electron CO_2 reduction.^{1–7} Among these, diiminetricarbonyl rhenium(1) complexes, including *fac*-ReCl(bpy)(CO)₃ where bpy = 2,2'-bipyridine, have been extensively investigated in both photocatalytic and electrocatalytic applications.^{8–20} Several recent examples of Re(1) complexes have used N-heterocyclic carbene (NHC)–aryl frameworks as redox-active ligands,^{21–25} but few have been examined for catalysis.^{26–30} In this work, we show that coupling with silicon nanowire (SiNW) photoelectrodes significantly improves the selectivity of Re(1)–NHC complexes in CO₂ reduction.

Recent reports by Delcamp and co-workers^{28,29} and Agarwal and co-workers³⁰ are among the few examples for CO_2 reduction using Re(i)–NHC compounds. In one of the studies by Delcamp and co-workers,²⁸ the efficacy of Re(i) complexes containing a NHC–pyridyl motif was recorded under irradiation with and without a molecular Ir(III) photosensitizer. The authors noted that the addition of an electron-deficient substituent on the NHC moiety improved photocatalytic performance.²⁸ Conversely, electron-deficient substituents on bpy often reduce the activity of ReCl(bpy)(CO)₃-type catalysts.^{31,32} In the study by Agarwal and



Fig. 1 Molecular structures of the Re(I)–NHC compounds under study: ReCl(*N*-methyl-*N*'-2-pyridylbenzimidazol-2-ylidine)(CO)₃ (1) and ReCl(*N*-methyl-*N*'-2-pyrimidylbenzimidazol-2-ylidine)(CO)₃ (2).

co-workers,³⁰ NHC–pyridyl and NHC–pyrimidyl ligands were employed, using a benzimidazole-based NHC. CO was observed as the primary electrolysis product (Faradaic efficiency \geq 60%), along with production of H₂ and HCOOH.

In this present report, we compare the performance of the latter two Re(1)–NHC compounds (1 and 2 in Fig. 1) under photoelectrochemical conditions. We demonstrate that utilizing SiNWs significantly improves selectivity towards CO over H₂ formation during solar-assisted CO₂ reduction, providing evidence that metal–NHC molecular catalysts may be successfully combined with this nanostructured material. The photoelectrode surface after catalysis are examined with diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) in order to explore interactions between the catalysts and SiNWs.

The synthesis, characterization, and electrocatalytic efficiency of compounds **1** and **2** have been previously reported.³⁰ As further confirmation, cyclic voltammograms were recorded for each Re(t)–NHC compound in acetonitrile with tetrabutylammonium hexafluorophosphate (TBAPF₆) as the supporting electrolyte. Aligned with prior work, two irreversible reduction waves were observed under Ar saturation for each compound at 100 mV s⁻¹, with peak currents at -2.06 V and -2.45 V for **1** (Fig. 2, potentials are *versus* Fc⁺/Fc), and at -1.91 and -2.30 V for **2** (see Fig. S1 in the ESI†). Under an atmosphere of CO₂, current enhancement was observed at both the first and second reduction waves. The current enhancement for **2** (Fig. S1, ESI†) is less significant than for **1** (Fig. 2).

Given the promising electrocatalytic activity exhibited by **1** and **2**, we sought to examine both compounds for photoelectrochemical

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Fig. 2 Cyclic voltammograms of $\mathbf{1}$ under (a) Ar and (b) CO₂ atmospheres on a glassy carbon electrode in acetonitrile.

 CO_2 reduction, since harnessing sunlight to drive CO_2 conversion is a compelling solution to utilize CO_2 . In particular, the photoelectrochemical approach eliminates the need for sacrificial donors by combining well-defined molecular catalysts with a photoactive electrode surface.^{33,34} Several molecular catalysts have been coupled with photoelectrodes for solar fuel production *via* CO_2 reduction.^{35–46} We employ SiNW photoelectrodes, which consist of vertically aligned arrays of SiNWs,⁴⁶ as the electron source for Re(t)-catalyzed CO_2 reduction in this research. The nanostructured morphology of SiNWs has been reported to be well-suited for high-efficiency solar energy applications.^{47,48}

Fig. 3 shows cyclic voltammograms of **1** recorded on a SiNW photoelectrode in acetonitrile under light irradiation provided by a Xe lamp. Under an atmosphere of Ar, the first reduction wave of **1** displays a peak current at -1.58 V (Fig. 3a), representing a photovoltage of 480 mV. A catalytic photocurrent is observed under CO₂ saturation (Fig. 3b), indicating that CO₂ reduction persists under photoelectrochemical conditions. The first reduction wave for 2 appears at -1.47 V, yielding a slightly lower photovoltage of 440 mV (Fig. S2, trace a, ESI†). A photocurrent enhancement was also observed under CO₂ (Fig. S2, trace b, ESI†), although less pronounced than for **1**, which matches the results under electrocatalytic conditions.³⁰

On the preparative scale at the potential of the first reduction, 1 and 2 displayed modest Faradaic efficiencies for CO production (FE_{CO} = 57% and 53%, respectively) in photoelectrolysis on SiNWs (Table S1, ESI[†]). Likely, residual water in the acetonitrile used in our study served as the proton source for CO₂ reduction. Complex 2 demonstrated excellent stability over four hours, while the photocurrent decayed gradually over time when 1 was used as the CO_2 -reduction catalyst (Fig. S3, ESI[†]). This is likely due to the relatively low photostability of **1**. In recent studies by Vaughan and co-workers, photochemical dissociation of CO was observed for a Re(I) NHC-pyridyl complex (similar to 1) but not for a Re(1) NHC-pyrimidyl complex (similar to 2).^{22,23} Nevertheless, more CO was produced by 1 in photoelectrolysis than by 2 (Fig. S4(c and d), ESI[†]), which is consistent with the more significant photocurrent enhancement observed for 1 at the first reduction potential (Fig. 3 and Fig. S2, ESI⁺).

The differing photochemical stability of 1 and 2 was further probed with surface analysis after photoelectrolysis. Specifically, the SiNWs were thoroughly washed with acetonitrile and dried at room temperature after being used for catalysis. Then, infrared spectra of the used SiNWs were collected on a DRIFTS spectrometer (Fig. 4). Prominent absorptions corresponding to surface-adsorbed Re(1) complexes are seen in the C-O stretching region of the collected spectra. For 2, these transitions appear at 2021 and 1918 cm^{-1} (Fig. 4b), and resemble the features of *fac*-ReCl(bpy)(CO)₃ grafted on silica surfaces found in our previous work.49,50 Moreover, the similarity of these bands to peaks of 2 collected from infrared spectroelectrochemistry (IR-SEC) at resting potential (2022, 1926, and 1899 cm⁻¹)³⁰ would suggest that the tricarbonyl moiety is retained after photoelectrolysis, assuming coalescence of the 1926 and 1899 cm⁻¹ peaks in the DRIFTS spectrum. In the infrared spectrum of SiNWs used with 1, two carbonyl bands are present at 2011 and 1879 cm^{-1} (Fig. 4a). Compared to previous IR-SEC data, these transitions are redshifted with respect to the starting complex (2020, 1923, and 1894 cm^{-1}),³⁰ which is consistent with structural changes during photoelectrolysis. This presumed degradation aligns with the aforementioned literature²² regarding the photostability of Re(1)-NHC complexes. From these data, we can conclude that 1 and 2 are strongly adsorbed to the SiNW surface, and that



(1000 mm) = 2001 mm = 1879 mm

Fig. 3 Cyclic voltammograms of **1** under (a) Ar and (b) CO_2 atmospheres on a SiNW photoelectrode in acetonitrile under light irradiation. The cyclic voltammogram under Ar on a glassy carbon electrode is also plotted for comparison (dotted trace, same as Fig. 2a).

Fig. 4 DRIFTS spectra of SiNWs used in photoelectrochemical CO_2 reduction using (a) **1** and (b) **2** in acetonitrile for 4 h.



Fig. 5 DRIFTS spectra of SiNWs used in photoelectrochemical CO_2 reduction using (a) **1** and (b) **2** in an acetonitrile solution containing 5% H₂O (by volume).

1 undergoes significant structural changes under photoelectrochemical conditions.

The introduction of Brønsted acids into the electrolyte is a popular technique to improve catalyst turnover.⁵¹ In our study, the presence of 5% H₂O (by volume) significantly improved CO₂-to-CO conversion using 1 and 2 on SiNWs (Fig. S4(a and b), ESI[†]), and yielded a new photocurrent for proton reduction (Fig. S5 and S6, ESI^{\dagger}). Consequently, the formation of H₂ was confirmed with product analysis during photoelectrolysis (Table S1 and Fig. S7, ESI^{\dagger}). For 1, the presence of 5% H₂O resulted in a lower Faradaic efficiency for CO production (FE_{CO} = 20%) along with significant H_2 formation (FE_{H₂} = 54%). Surface analysis of SiNWs after photoelectrolysis showed a negligible amount of surface-adsorbed 1 (Fig. 5a). Control experiments confirmed that the addition of 5% H₂O had negligible effect on the photostability of 1 or 2. These observations imply that the presence of 5% H₂O inhibited the adsorption of 1 on SiNWs and subsequent electron transfer from SiNWs to 1 for CO₂-to-CO conversion. In addition, the photocurrent obtained for 1 displayed a time course profile (Fig. S8, trace a, ESI⁺) similar to that of H₂ production (Fig. S7, trace a, ESI⁺), suggesting that proton reduction dominated in the presence of H₂O.

Conversely, 2 displayed a Faradaic efficiency of 68% for CO production after the addition of H_2O , with only minor quantities of H_2 (FE_{H₂} = 9%). After photoelectrolysis with 2, surface analysis with DRIFTS showed infrared absorptions at 2021 and 1918 cm⁻¹ (Fig. 5b), indicating the presence of strongly adsorbed 2 on SiNWs even with 5% H_2O added to the aceto-nitrile solution. In the absence of the Re(I) catalysts, the values of FE_{H₂} on the SiNW photoelectrode were measured to be 0% in acetonitrile and 49% in an acetonitrile solution containing H_2O . These results suggest that in our system CO₂ reduction is mediated by the Re(I) catalysts while proton reduction mainly occurs on the SiNW surface.

Complexes 1 and 2 were also tested in photocatalytic CO_2 reduction using a molecular photosensitizer, $Ru(dmb)_3^{2+}$ where dmb is 4,4'-dimethyl-2,2'-bipyridine, and triethanolamine as a sacrificial electron donor in acetonitrile. Under light irradiation, the two Re(I)–NHC complexes demonstrated similar reactivity

(Table S1, ESI[†]). Using 2 as a catalyst led to a slightly higher turnover number for CO production than using 1, but significant H₂ formation (H₂/CO ~ 0.5) was observed for both catalysts. Therefore, the SiNW photoelectrode appears to be a better energy source for the Re(1)–NHC catalysts than the Ru(dmb)₃²⁺ photosensitizer to selectively drive CO₂ reduction over proton reduction. We expect that CO₂ reduction using the Re(1) catalysts on SiNWs could be further improved by employing a two-compartment cell which separates the SiNW photoelectrode from the counter electrode, constantly stirring the reaction solution, and carrying out photoelectrolysis for a longer period of time.

In summary, the presence of strongly adsorbed Re(I)-NHC complexes on the SiNW photoelectrode surface is clearly associated with selective CO₂-reduction catalysis. We expect that both the efficiency and selectivity in solar fuel generation could be enhanced by tuning the interactions between molecular catalysts and photoelectrode surfaces. Further studies are underway to test this hypothesis.

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