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# Photoelectrochemical CO<sub>2</sub> Reduction by a Molecular Cobalt(II) Catalyst on Planar and Nanostructured Si Surfaces

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**Abstract:** In the presence of a molecular Co(II) catalyst, CO<sub>2</sub> reduction occurred at much less negative potentials on Si photoelectrodes than on an Au electrode. The addition of 1% H<sub>2</sub>O significantly improved the performance of the Co(II) catalyst. Photovoltages of 580 mV and 320 mV were obtained on Si nanowires and a planar Si photoelectrode, respectively. This difference likely originated from the fact that the multi-faceted Si nanowires are better in light harvesting and charge transfer than the planar Si surface.

Photochemical reduction is a promising approach towards sustainable CO<sub>2</sub> utilization since this process employs natural sunlight as a renewable energy input.<sup>[1]</sup> Both heterogeneous<sup>[2]</sup> and homogeneous systems<sup>[3]</sup> have been extensively investigated in attempts to achieve efficient CO<sub>2</sub>-to-fuel conversion under photochemical conditions. Homogeneous molecular catalysts could be highly efficient in mediating multielectron CO<sub>2</sub> reduction. However, the most active homogenous CO<sub>2</sub>-reduction catalysts<sup>[4]</sup> are often based on rare-earth metals, and great efforts have been made to seek for catalysts with high activities based on earth-abundant materials.<sup>[5]</sup>

Among these homogeneous catalysts are coordination complexes of cobalt.<sup>[5a, 6]</sup> For instance, Chan *et al.*<sup>[5a]</sup> recently reported photochemical CO<sub>2</sub> reduction by a molecular catalyst, [Co(TPA)CI]CI where TPA is tris(2-pyridylmethyl)amine. An Ir(III) photosensitizer was employed to harvest light and transfer electrons to [Co(TPA)CI]CI in the presence of triethylamine as a sacrificial electron donor. Yang *et al.*<sup>[7]</sup> synthesized a cyclometalated Ir(III) complex as a photosensitizer for photochemical CO<sub>2</sub> reduction. In both studies, high turnover numbers and reasonable selectivity towards CO formation were obtained. However, molecular complexes of rare-earth metals were needed as photosensitizers to harvest light for this and many other molecular catalysts,<sup>[8]</sup> which significantly increases the cost.

Light-absorbing solid-state materials, including inorganic semiconductors and metal-organic frameworks,<sup>[9]</sup> have been utilized as photosensitizers based on abundant materials for molecular catalysts.<sup>[10]</sup> For example, Jin *et* 

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al.<sup>[11]</sup> deposited a macrocyclic cobalt catalyst onto different titanium dioxide surfaces for use in photochemical CO<sub>2</sub> reduction. The researchers demonstrated that titanium dioxide nanoparticles served to absorb UV light while the surface cobalt catalyst was responsible for reducing CO<sub>2</sub> to CO. Several molecular catalysts have been coupled with photoelectrodes for solar fuel production via CO<sub>2</sub> reduction.<sup>[12]</sup> This photoelectrochemical approach combines light-harvesting materials with homogeneous catalysts, and eliminates the need for amine-based sacrificial electron donors that are often required in photochemical CO<sub>2</sub> reduction.

Herein, we show photoelectrochemical  $CO_2$  reduction by a system based on earth-abundant elements, in which Si photoelectrodes serve as robust photosensitizers for [Co(TPA)CI]CI. In addition, we investigate the effects of H<sub>2</sub>O addition and photoelectrode morphology on photoelectrochemical  $CO_2$  reduction using the Co(II) catalyst.

The molecular Co(II) complex was synthesized following an established procedure.<sup>[13]</sup> Characterization with UV-visible, <sup>1</sup>H NMR, and infrared spectroscopies (Figures S1-S3 in Supporting Information) and comparison with results in the literature<sup>[5a]</sup> indicate the synthesized Co(II) complex has a trigonal bipyramidal geometry. Under an atmosphere of Ar, two irreversible redox waves were observed with reduction peaks at -1.93 V and -2.15 V (all the potentials mentioned in this report are versus Fc<sup>+</sup>/Fc) in the cyclic voltammogram (CV) of [Co(TPA)CI]CI obtained on an Au electrode (Figure 1). Corresponding oxidation peaks are also clearly observed. These two waves are assigned to the Co<sup>II</sup>/Co<sup>I</sup> and Co<sup>I</sup>/Co<sup>0</sup> redox couples, respectively.<sup>[5a]</sup> Significant current enhancement was observed when the same solution was saturated with CO<sub>2</sub>, indicating that the Co(II) complex is a potential catalyst for electrochemical CO<sub>2</sub> reduction. Under CO<sub>2</sub>, the oxidation peaks disappeared since the electrochemically generated species, such as Co(I), were oxidized upon reducing  $CO_2$  molecules.



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Figure 1. Cyclic voltammograms of [Co(TPA)Cl]Cl under Ar (gray) and  $CO_2$  (blue) on an Au electrode. Supporting electrolyte 0.1 M TBAPF<sub>6</sub> in acetonitrile, scan rate 100 mV/s.

Adding a small amount of  $H_2O$  to the acetonitrile solution of [Co(TPA)CI]CI altered its redox properties. In our study, proton reduction by reduced cobalt species was observed in the CVs collected in the presence of 1%  $H_2O$  (by volume), although the reduction potentials did not change significantly (Figure S4). We note that while CO<sub>2</sub> reduction occurs readily at the first reduction potential of [Co(TPA)CI]Cl (Figure 1), proton reduction is likely mediated by Co<sup>0</sup> species as indicated by the CV collected under Ar (Figure S4). This may explain the excellent selectivity towards CO formation in CO<sub>2</sub> reduction by [Co(TPA)CI]Cl observed in Chan's study<sup>[5a]</sup> and in our work.

Furthermore, the addition of 1% H<sub>2</sub>O resulted in significantly greater current enhancement (2.7-fold in Figure S4 vs 2.0-fold in Figure 1) when the solution of [Co(TPA)CI]CI was saturated with CO<sub>2</sub>. This comparison suggests that the addition of 1% H<sub>2</sub>O promotes CO<sub>2</sub> reduction by the Co(II) catalyst. Detailed study of the reaction mechanisms in the presence of H<sub>2</sub>O is still under investigation.

However, this Co(II) catalyst is only active at highly negative potentials in electrochemical  $CO_2$  reduction (Figure 1). The potential for two-electron reduction of CO<sub>2</sub> to CO is -0.53 V versus NHE at pH 7 (corresponding to -1.17 V vs Fc<sup>+</sup>/Fc),<sup>[14]</sup>, suggesting an overpotential of ~800 mV using the Co(II) catalyst. Photovoltaic effects of some semiconductors have been utilized to achieve CO<sub>2</sub> reduction at modest potentials.<sup>[12e-k]</sup> For example, Kumar et al.<sup>[12e]</sup> investigated CO<sub>2</sub> reduction by a molecular Re(I) catalyst on a p-type Si photoelectrode. Selective reduction of CO2 to CO was observed at a potential ~600 mV less negative than that required on a Pt electrode. Recent work by Liu et al.[15] demonstrated successful applications of Si nanowires (SiNWs) in high-efficiency solar energy conversion. In this present study, we couple the Co(II) catalyst with an SiNWs photoelectrode consisting of vertically aligned arrays of SiNWs (Figure 2) for use in photoelectrochemical CO2 reduction. In the absence of the Co(II) catalyst, a much lower photocurrent was observed on the SiNWs photoelectrode (Figure S5).



Figure 2. SEM images of an SiNWs photoelectrode: (a) side view and (b) top view.

A Xe lamp was used to provide simulated solar irradiation for SiNWs in our photoelectrochemical studies. In dry acetronitrile, multiple broadened redox peaks are present in the CV collected on SiNWs under Ar (Figure 3, see also trace a in Figure S6) in comparison to two distinct redox waves on the Au electrode (Figure 1). This broadening in the reduction peaks is likely due to the heterogeneity of the SiNWs, which are multifaceted nanowires with a variety of crystal planes exposed.<sup>[15b]</sup> The various crystal plans might differ in light harvesting and electrontransfer kinetics. Under an atmosphere of  $CO_2$ , significant enhancement in photocurrent is observed on SiNWs in a wide range of potentials (Figure 3). This enhancement in photocurrent is likely associated with  $CO_2$  reduction by  $Co^{I}$  species.



Figure 3. Cyclic voltammograms of [Co(TPA)CI]Cl in dry acetonitrile on an SiNWs photoelectrode under Ar (gray) and  $CO_2$  (green). Supporting electrolyte 0.1 M TBAPF<sub>6</sub>, scan rate 100 mV/s.

The advantages of using SiNWs over the Au electrode were clearly demonstrated in the presence of H<sub>2</sub>O. In the CV collected under Ar (Figure S6, trace b), the first reduction corresponding to the Co<sup>ll</sup>/Co<sup>l</sup> redox couple occurs at -1.35 V (determined at maximum photocurrent), representing a photovoltage of 580 mV as a result of light irradiation compared to that on the Au electrode. The second reduction occurs around -1.65 V as a shoulder to a proton reduction peak at -1.94 V. A significant photovoltage was also observed using a planar Si photoelectrode which contains the Si(100) crystal plane. On planar Si, the two reduction waves of [Co(TPA)CI]Cl overlap significantly (Figure S6, trace c), but occur in a much narrower potential range than on SiNWs. This is attributed to the fact that only the (100) crystal plane is present on the planar Si surface while the SiNWs are multifaceted. The presence of 1% H<sub>2</sub>O resulted in anodic potential shifts in the reduction potentials of [Co(TPA)CI]CI on the planar Si photoelectrode. In addition, the Co<sup>ll</sup>/Co<sup>l</sup> reduction wave was observed at around -1.61 V (Figure S6, trace d) indicating a photovoltage of 320 mV compared to that on the Au electrode.

In the presence of 1% H<sub>2</sub>O, CO<sub>2</sub> reduction was observed at -1.57 V on SiNWs (Figure 4c), compared to -1.80 V on planar Si (Figure 4b, also Figure S7) and -1.96 V on Au (Figure 4a). Therefore, the use of SiNWs is advantageous since it allows CO<sub>2</sub> reduction at a less negative potential than using the planar Si photoelectrode and the Au electrode. The comparison shown in Figure 4 is similar to the previous study of a Ni(II) catalyst on Si photoelectrodes by Liu *et al.*<sup>[15b]</sup> We attribute this effect of photoelectrode geometry to the unique multifaceted feature and excellent light harvesting of SiNWs. Other contributing factors include the greater surface area of SiNWs in comparison with the planar Si photoelectrode, orthogonal light absorption and charge transfer directions in SiNWs.

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Figure 4. Cyclic voltammograms of [Co(TPA)Cl]Cl in an acetonitrile solution containing 1% H<sub>2</sub>O on (a) Au, (b) planar Si, and (c) SiNWs under  $CO_2$ . Supporting electrolyte 0.1 M TBAPF<sub>6</sub>, scan rate 100 mV/s.

We estimate an optimal H<sub>2</sub>O content to be ~1-2% for CO<sub>2</sub> reduction by [Co(TPA)CI]CI on SiNWs. At higher H<sub>2</sub>O contents (>5% by volume), the peak associated with CO2-reduction catalysis became less distinct as proton reduction starts to dominate (Figure S8). Bulk electrolysis was carried out in an acetonitrile solution containing 1% H<sub>2</sub>O and 1 mM [Co(TPA)CI]CI on the photoelectrodes under an atmosphere of CO<sub>2</sub>. Faradaic efficiencies for CO formation were measured to be 69% and 57% on SiNWs and planar Si, respectively. Formation of H<sub>2</sub> (Faradaic efficiencies 26% and 22%, respectively) was also observed. In our study, the production of CO from CO<sub>2</sub> using [Co(TPA)CI]CI on SiNWs was confirmed by infrared spectroscopy combined with isotope labeling (Figure S9). On the SiNW photoelectrode, a turnover number of ~4.2 was obtained for CO production after bulk electrolysis of a solution containing 10 µmol [Co(TPA)CI]CI on SiNWs for 4.6 hours (Figure S10).

During bulk electrolysis in the presence of 1% H<sub>2</sub>O, the photocurrent generated on SiNWs showed negligible decay over a period of 5 h (Figure S11). In addition, heterogeneous deposition of the Co(II) catalyst was not observed under the experimental conditions, as shown by microscopic images of SiNWs collected before and after bulk electrolysis for 3 h (Figure S12). The stability of [Co(TPA)CI]CI was further confirmed by surface analysis of SiNWs with X-ray photoelectron spectroscopy (XPS). In particular, a fresh SiNW photoelectrode was soaked in the electrolysis solution in the dark. The XPS spectrum of this soaked photoelectrode was then collected and compared with that of a photoelectrode used in bulk electrolysis. Spectra of these two photoelectrodes were found to be almost identical (Figure S13), indicating that the Co(II) catalyst remained intact during bulk electrolysis. Our results suggest that a robust system based on abundant materials for CO2-to-fuel conversion could be developed using the combination of the Co(II) catalyst and the SiNWs photoelectrode.

In summary, we have demonstrated that Si photoelectrodes are viable solid-state photosensitizers for a molecular Co(II) catalyst in CO<sub>2</sub> reduction. The use of SiNWs is advantageous since it allows CO<sub>2</sub> reduction at less negative potentials than using planar Si due to the unique multifaceted feature of SiNWs. The addition of a small amount of H<sub>2</sub>O enabled CO<sub>2</sub> reduction with less applied bias. Further studies with electrochemistry and spectroscopy are underway to elucidate how H<sub>2</sub>O alters CO<sub>2</sub>reduction catalysis by [Co(TPA)CI]CI on SiNWs.

#### **Experimental Section**

The UV-visible spectrum of [Co(TPA)CI]CI in acetonitrile was obtained on a Cary 50 Bio spectrophotometer. Infrared spectra were recorded on a Thermo Nicolet 6700 spectrometer. The morphology of SiNWs was analyzed with a JOEL JSM 6340F scanning electron microscope. Cyclic voltammograms were collected on a PAR model VersaSTAT 4 potentiostat using a single compartment cell. Conditions for electrochemical studies are: supporting electrolyte 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF<sub>6</sub>) in acetonitrile, scan rate 100 mV/s, an Au working electrode, a Pt counter electrode, and a non-aqueous Ag/AgNO $_3$  reference electrode. The electrochemical cell was purged with Ar or CO2 (99.999%, Airgas) for 20 min before every scan. In controlled potential experiments, cyclic voltammograms were collected prior to bulk electrolysis studies using 10 mL of 1 mM [Co(TPA)CI]CI, 0.1 M tetrabutylammonium hexafluorophosphate, and 1% H<sub>2</sub>O (by volume) in acetronitrile. Bulk electrolysis was carried out in an Hshape electrochemical cell, in which the working electrode was separated from the counter electrode by a sintered glass frit. Prior to bulk electrolysis using the SiNWs and planar Si photoelectrodes, the solution was bubbled with CO2 for 20 min. The solution was then irradiated with a 300 W xenon lamp equipped with a water filter. Light intensity was kept at 113 mW/cm<sup>2</sup>. The headspace above the reaction solution was sampled with a gas-tight syringe at different time intervals for product analysis using an Agilent 7820 GC equipped with a TCD detector and a 60/80 Carboxen-1000 packed column (Supelco).

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Photoelectrochemical  $CO_2$  reduction was achieved by coupling a molecular Co(II) catalyst with Si photoelectrodes. The presence of a small amount of water significantly improved the performance of the Co(II) catalyst. A much greater photovoltage was obtained on Si nanowires than on a planar Si photoelectrode due to the multi-faceted feature and better light harvesting of Si nanowires.

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