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COMMUNICATION

Tunable, light-assisted co-generation of CO and H_2 from CO_2 and H_2O by Re(bipy-tbu)$(CO)_3Cl$ and p-Si in non-aqueous medium†‡

Bhupendra Kumar,[a] Jonathan M. Smieja,[b] Alissa F. Sasayama[b] and Clifford P. Kubiak*[ab]

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The light-assisted co-generation of carbon monoxide and hydrogen from carbon dioxide and water is reported. The combination of a homogeneous CO-evolving electrocatalyst and a heterogeneous H_2-evolving photoelectrode surface provides for tunability of the H_2/CO ratio. A total Faradaic efficiency of 102 ± 5% and a H_2/CO ratio of 2 : 1 were achieved at a low homogeneous catalyst concentration (0.5 mM) in acetonitrile/water mixtures.

The co-generation of carbon monoxide (CO) and hydrogen (H_2) is an important step in the synthesis of renewable fuels.[1,2] This mixture, commonly referred to as synthesis gas (or syngas), can be fed into the Fischer–Tropsch process to make synthetic liquid fuels.[3] These fuels can be used in the transportation sector or for storage of intermittent energy from renewable sources such as solar and wind. Over the past three decades considerable research has been performed on both carbon dioxide (CO_2) reduction electrocatalysts[4–6] and proton reduction electrocatalysts.[7–9] This research, however, has been devoid of significant findings on the co-generation of CO and H_2. It is often the case that a catalyst for the reduction of protons to H_2 will be poisoned by the CO produced by the reduction of CO_2, or that a catalyst for the reduction of CO_2 to CO will not be able to compete with hydrogen production in the presence of proton sources. Although syngas can be produced from CO *via* the water-gas-shift (WGS) reaction or from H_2 *via* the reverse water-gas-shift (rWGS) reaction, it is desirable to employ a system to achieve the intended ratio of gases in one step and thus eliminate the inefficiencies of multiple process integration.

There are a very few reports of simultaneous CO_2 and H_2O reduction to syngas. Recently, electrochemical[10] and thermochemical[11,12] methods have been reported to reduce CO_2 and H_2O simultaneously. In the electrochemical method, water and CO_2 were electrochemically reduced at a silver cathode at a potential of approximately −2.00 V *vs.* SCE.[10] The thermochemical method consists of two steps: (1) thermal dissociation of ZnO to Zn (or Fe_3O_4 to FeO) using concentrated solar radiation (endothermic process) and (2) the reduced Zn (or FeO) reacts with H_2O and CO_2 to generate ZnO (or Fe_3O_4) together with syngas (exothermic process).[11,12]

Previously we reported the two-electron electrocatalytic reduction of CO_2 to CO by Re(bipy-tBu)$(CO)_3Cl$ (where bipy-tBu = 4,4′-di-*tert*-butyl-2,2′-bipyridine) in acetonitrile with high turnover frequency, high turnover number, and a Faradaic efficiency of 99 ± 2%.[13] That work, reported on a glassy carbon electrode, was then followed up by work with the same catalyst on a p-Si photoelectrode surface. In that study we showed the photoelectrochemical reduction of CO_2 to CO with a photovoltage of more than 500 mV and a Faradaic efficiency 97 ± 3%.[14]

Here we report the successful coupling of a homogeneous catalyst for the reduction of CO_2 with heterogeneous water reduction by illuminated p-Si (Fig. 1). In this system, the homogeneous CO_2 reduction and heterogeneous water reduction are in direct competition for photo-generated electrons from the cathode. This feature provides for a tunable co-generation of CO and H_2 through variation of homogeneous catalyst concentration and through addition of water. This system has the ability to produce synthesis gas in the desired H_2/CO ratio of 2 : 1 with high overall Faradaic efficiency. The photoelectrochemical (PEC) cell used in these experiments has been described.[14]

The characteristic behavior of the p-Si/Re(bipy-tBu)$(CO)_3Cl$ molecular catalyst junction, where both the first and second

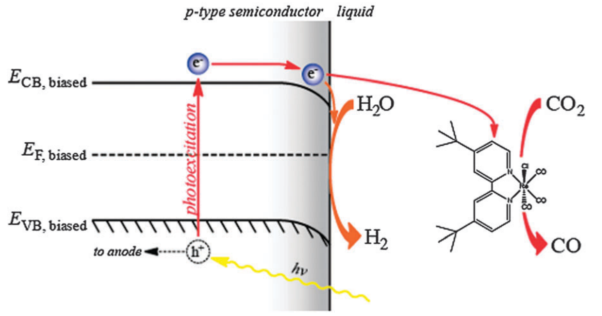

Fig. 1 Schematic representation for light-assisted co-generation of H_2 and CO at biased illuminated p-Si by heterogeneous H_2O reduction (depicted by orange arrows) at the p-Si surface and homogeneous reduction of CO_2 by Re(bipy-tBu)$(CO)_3Cl$ (where bipy-tBu = 4,4′-di-*tert*-butyl-2,2′-bipyridine) (depicted by red arrows), respectively.

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[a] *Materials Science and Engineering Program, University of California San Diego, 9500 Gilman Drive MC 0418, La Jolla, California 92093, USA*
[b] *Department of Chemistry and Biochemistry, University of California San Diego, 9500 Gilman Drive MC 0358, La Jolla, California 92093, USA. E-mail: ckubiak@ucsd.edu; Fax: +1 858 534 5383; Tel: +1 858 822 2665*

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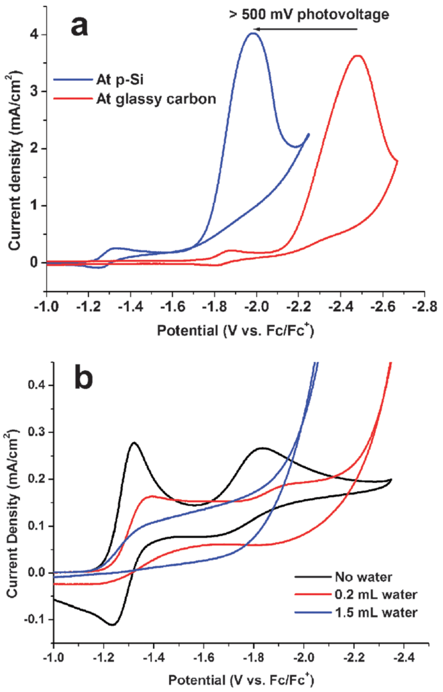

Fig. 2 (a) Re(bipy-tBu)(CO)$_3$Cl electrochemistry under a CO_2 atmosphere on both glassy carbon and p-Si working electrodes showing more than 500 mV of photovoltage at illuminated p-Si 0.5 mM catalyst, 0.1 M TBAH electrolyte, Pt counter electrode, 100 mV s^{-1} scan rate. (b) Cyclic voltammograms of 1 mM Re(bipy-tBu)(CO)$_3$Cl in 30 mL of acetonitrile on the illuminated p-Si photocathode without water addition (black), 0.4 M (0.2 mL) water (red) and 2.6 M (1.5 mL) water (blue).

reductions of the Re complex on illuminated p-Si are 530 mV more positive than at metal electrodes (Pt or glassy carbon) under an argon atmosphere, is shown in Fig. S1 (ESI‡). In the presence of CO_2, there is a large increase in current in the second reduction of the complex, which is assigned to the homogeneous reduction of CO_2 to CO at both the p-Si photocathode and the glassy carbon cathode as shown in Fig. 2a. The kinetically limited photocurrent density for homogeneous CO_2 reduction at p-Si is modulated by incoming light intensity (Fig. S2, ESI‡). Upon addition of deoxygenated water under an argon atmosphere, the cyclic voltammogram of the p-Si/Re(bipy-tBu)(CO)$_3$Cl molecular catalyst junction (under illumination) loses its characteristic reduction peaks (Fig. 2b). Under these conditions the Re(bipy-tBu)(CO)$_3$Cl reduction peaks are obscured by a broad reduction feature in the range of −1.38 to −1.78 V *vs.* Fc/Fc$^+$. It was also observed, as expected, that the addition of water narrowed the electrochemical window due to the reduction of protons from water to H_2. A similar feature was observed on p-Si under illumination in acetonitrile upon addition of water with no Re(bipy-tBu)(CO)$_3$Cl. Gas chromatography of the head space after a bulk electrolysis experiment run at −1.65 V *vs.* Fc/Fc$^+$ with and without Re(bipy-tBu)(CO)$_3$Cl under an argon atmosphere showed only hydrogen production. This confirms that the water reduction to hydrogen in this system is in fact heterogeneous reduction of water in a non-aqueous medium at illuminated p-Si.

Bradley *et al.* reported the photoelectrochemical reduction of tetraazomacrocyclic metal complexes on illuminated p-Si[15] and they were later shown to catalyze the photoreduction of CO_2 to CO on p-Si.[16] This system achieved its best results with 18 mM $[(Me_6[14]aneN_4)Ni^{II}]^{2+}$ in a 1 : 1 acetonitrile–water solution with 0.1 M $LiClO_4$ as the supporting electrolyte. Under these conditions, a H_2/CO ratio of 0.5 and a Faradaic efficiency of 95 ± 5% were obtained. In our work, the ratio of H_2/CO can be increased from 0.4 to 1.2 as the water content is increased from 1% to 5% (by volume) with 5 mM Re(bipy-tBu)(CO)$_3$Cl. The Faradaic efficiencies in those cases are between 90 ± 5% and 100 ± 5% for co-generation. Further addition of water did not change the H_2 to CO ratio at a catalyst concentration of 5 mM. It should be noted that the concentration of CO_2 in acetonitrile/water stays constant up to a water concentration of 3 M, but for concentrations of water higher than that the CO_2 solubility in acetonitrile decreases considerably.[17] To fully utilize the activity of Re(bipy-tBu)(CO)$_3$Cl for reduction of CO_2 to CO, therefore, the water concentration must be kept at or below 3 M. In addition, at higher concentrations of water both tetrabutylammonium hexafluorophosphate (TBAH, electrolyte) and Re(bipy-tBu)(CO)$_3$Cl are not fully soluble.

At a high Re(bipy-tBu)(CO)$_3$Cl concentration, the molecular catalyst is able to compete with the heterogeneous water reduction at illuminated p-Si even at water concentrations (2.5 M) much higher than the CO_2 concentration (0.28 M in acetonitrile at one atmosphere of CO_2).[17] To achieve a H_2/CO ratio of 2 : 1

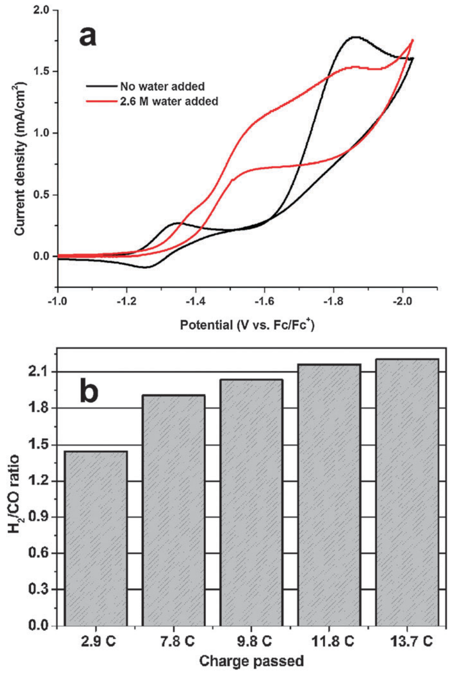

Fig. 3 (a) Water addition to 0.5 mM Re(bipy-tBu)(CO)$_3$Cl in 40 mL of acetonitrile under CO_2 at illuminated p-Si results in a distortion of the voltammogram's shape and a redistribution of current as a result of heterogeneous water reduction to hydrogen gas; without water (black) and 2.6 M (2 mL) water added (red). Intermediate additions of water are omitted for clarity in this figure, but show a gradual distortion of the CV trace. (b) Chart shows the ratio of H_2 to CO with increase in charge passed during bulk electrolysis. 2 : 1 H_2/CO is near the ideal ratio for most cobalt-based Fischer–Tropsch systems and provides for the highest possible percentage of liquid fuel molecules.

(a ratio suitable for liquid fuel formation by the Fischer–Tröpsch process) the Re complex concentration was decreased from 5 mM to 0.5 mM. Fig. 3a shows the effect of water in an illuminated p-Si/Re(bipy-tBu)$(CO)_3Cl$ junction system under an atmosphere of CO_2. Initial addition of a small amount of water lowers the catalytic current density at the 2nd reduction of Re(bipy-tBu)-$(CO)_3Cl$. At higher concentrations of water, the decrease in homogeneous CO_2 reduction by Re(bipy-tBu)$(CO)_3Cl$ is compensated for by heterogeneous water reduction at illuminated p-Si so that the catalytic current density recovers. Co-generation of H_2 and CO was confirmed by simultaneous detection in a split column gas chromatograph (GC). The H_2 to CO ratio could then be calculated quantitatively from the number of moles of H_2 and CO produced by comparing GC peak areas with calibration curves. Fig. 3b shows consistent co-generation of H_2 and CO with a ratio near 2 : 1 during bulk electrolysis experiments run at a potential of −1900 mV *vs.* Fc/Fc^+.

Control experiments were conducted with glassy carbon as the working electrode under the same conditions as those described above and H_2/CO ratios of only 1 : 7 (or 0.14) were observed. This experiment confirms the role of p-Si as the heterogeneous catalyst for H_2 production from water and the role of Re(bipy-tBu)$(CO)_3Cl$ as the only CO_2 reduction catalyst.

The gas chromatographs of CO and H_2 are shown in Fig. S3 and S4 (ESI‡). As the amount of charge passed during bulk electrolysis is increased from 0 to 13.7 C, the total area of both the CO and H_2 peaks increased linearly. Fig. S5a (ESI‡) shows that the increase in charge passed is linear with time during bulk electrolysis, indicating little to no degradation of the catalysts during the course of the experiment. Dividing the slope of the curve in Fig. S5a (ESI‡) by the area of the electrode gives a current density for CO and H_2 co-generation of 5.6 mA cm^{-2}. There is a linear relationship between the total number of moles of electrons passed during bulk electrolysis and the total number of moles of gas (H_2 + CO) with a slope 1.94 (indicative of both CO_2 and water reduction being two electron processes) as shown in Fig. S5b (ESI‡). Based on Fig. S5b, the Faradaic efficiency for co-generation of H_2 and CO under these conditions is 102 ± 5%.

In the three electrode set-up for the cathodic half reaction only, the total light-to-chemical energy conversion efficiency for CO_2 and water photoreduction is given by:[18,19]

$$\eta = \frac{J_\mathrm{m}\left[\sum_i \xi_i\left\{\left(\frac{\Delta H_i}{Z_i}\right) - V_{i,\mathrm{op}}\right\}\right] - \{\text{IR loss}\}}{I_{h\nu}} \qquad (1)$$

where J_m = catalytic current density, ξ_i = Faradaic efficiency, ΔH_i = heat of combustion, Z_i = number of electrons involved in the reduction, $V_{i,\mathrm{op}}$ = overpotential, IR loss = loss associated with non-Faradaic processes, and $I_{h\nu}$ = incoming light intensity (power density). In the above approach, fuels produced as a result of CO_2 and water reduction are considered mainly as thermal combustion fuels. The ΔH_i for CO and H_2 are 2.93 eV $coulomb^{-1}$ and 2.96 eV $coulomb^{-1}$, respectively, and the overpotential for CO generation is 1.25 V with a Faradaic efficiency of 32%. In the case of water reduction, the thermodynamic potential of proton reduction to hydrogen in acetonitrile with water as the proton source is not available in the literature. Therefore, the thermodynamic potential (−1.46 V *vs.* Fc/Fc^+) of proton reduction with acetic acid (weak acid) as the proton source in acetonitrile was used in the conversion efficiency calculation as the thermodynamic potential for water reduction.[20] Therefore, the overpotential for H_2 generation is 0.44 V. The co-generation process has a Faradaic efficiency of nearly 100%, so IR loss is zero in this case. With a monochromatic light (661 nm) illumination intensity of 95 mW cm^{-2} on the photocathode surface and a catalytic current density of 5.6 mA cm^{-2}, the total light-to-chemical energy conversion efficiency for the cathodic half cell reaction calculated by eqn (1) is 4.6%.

Here we have shown the efficient co-generation of CO and H_2 from CO_2 and H_2O in a mixed homogeneous/heterogeneous system that allows for tunability in product distribution. We are able to tune the H_2/CO ratio from 0 to 2 : 1 by addition of water and variation of Re(bipy-tBu)$(CO)_3Cl$ concentration. To our knowledge this is the first example of co-generation of this type and may provide for opportunities to co-generate H_2 and CO in the future at lower overpotential and higher overall light-to-chemical energy conversion efficiency. Further studies are ongoing in our laboratory to further optimize the system through catalyst and surface optimization.

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