Photochemistry *Hot Paper*

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Selective Photoelectrochemical Reduction of Aqueous CO_2 to CO by Solvated Electrons**

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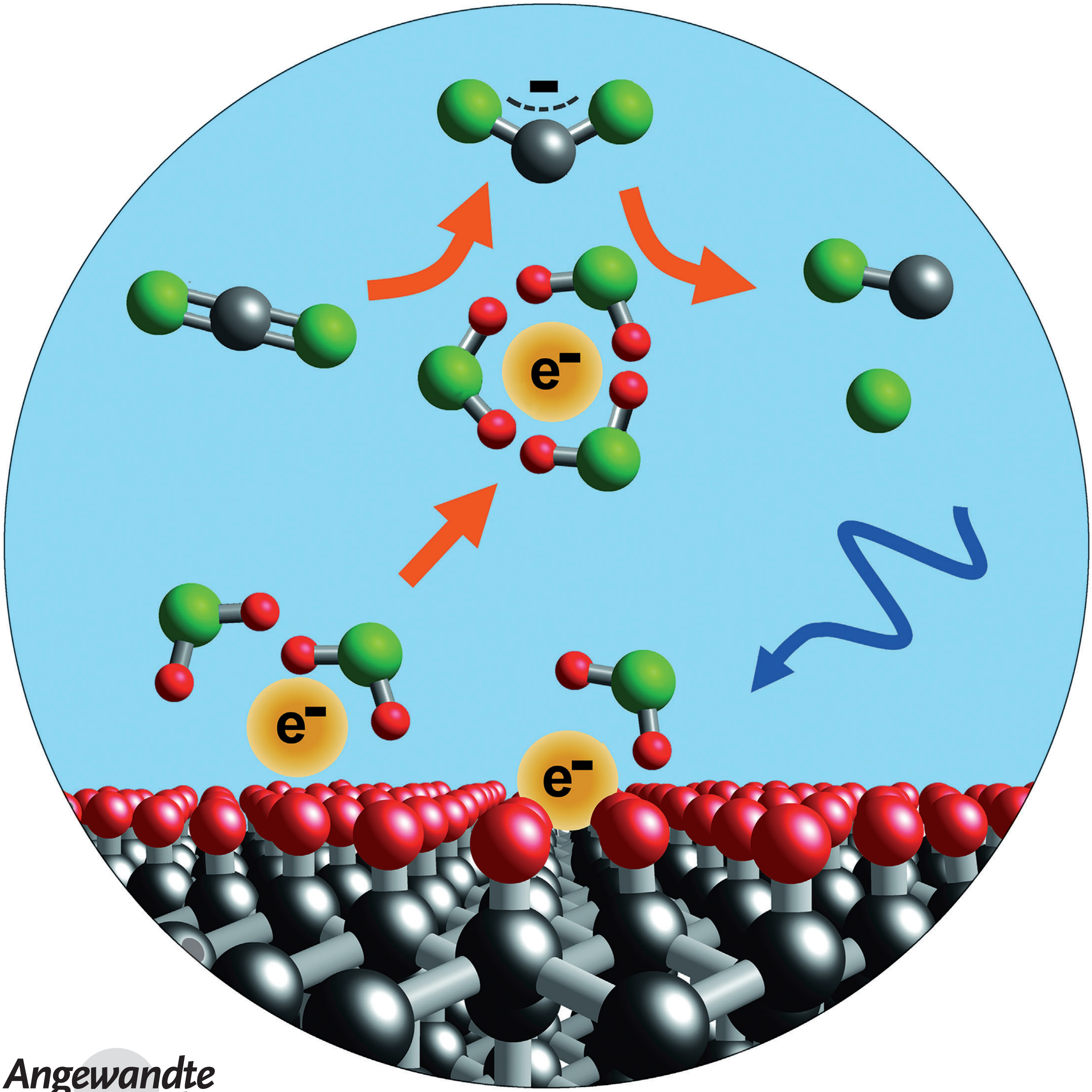

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***Abstract:** Reduction of CO_2 by direct one-electron activation is extraordinarily difficult because of the -1.9 V reduction potential of CO_2. Demonstrated herein is reduction of aqueous CO_2 to CO with greater than 90 % product selectivity by direct one-electron reduction to $CO_2^{\bullet -}$ by solvated electrons. Illumination of inexpensive diamond substrates with UV light leads to the emission of electrons directly into water, where they form solvated electrons and induce reduction of CO_2 to $CO_2^{\bullet -}$. Studies using diamond were supported by studies using aqueous iodide ion (I^-), a chemical source of solvated electrons. Both sources produced CO with high selectivity and minimal formation of H_2. The ability to initiate reduction reactions by emitting electrons directly into solution without surface adsorption enables new pathways which are not accessible using conventional electrochemical or photochemical processes.*

The development of methods to efficiently convert atmospheric CO_2 into chemical feedstocks or other environmentally benign products is one of the most pressing problems today. Attempts to reduce CO_2 under aqueous conditions by photochemical and electrochemical methods typically yield poor selectivity and poor efficiency because of competing reduction of H^+ to H_2, as well as the many possible coupling reactions which can occur on the electrode surface.[1] The vast majority of work on CO_2 photoreduction has focused on proton-coupled electron-transfer (PCET) reactions,[2] which usually require the participation of multiple electrons and protons as well as long-lived intermediates, and are therefore inefficient. A much more direct and more efficient pathway would be the one-electron reduction of CO_2 into $CO_2^{\bullet -}$. This pathway has been little studied photochemically because the one-electron reduction, $e^- + CO_2 \rightarrow CO_2^{\bullet -}$, has a standard redox potential (E^0) of -1.9 V versus the standard hydrogen electrode (SHE).[1] This value lies above the conduction band edge of nearly all semiconductors,[3] thus rendering them unable to initiate the one-electron reduction process.[1,4]

Herein, we demonstrate a new approach to CO_2 reduction using aqueous solvated electrons, and show that solvated electrons produced by illuminating diamond surfaces selectively reduce CO_2 into CO with high product selectivity and minimal proton reduction. To enable this new pathway, we build on recent work showing that inexpensive, commercial-grade diamond samples can act as facile solid-state sources of solvated electrons in water when illuminated with ultraviolet light. The possible role of solvated electrons in photochemical reduction on diamond has been inferred previously,[5] but until our recent work on N_2 reduction[6] the direct role of solvated electrons in important reduction reactions had not been established. Unlike conventional electrochemical or photochemical approaches where reactants must adsorb to a surface, this approach does not require surface adsorption and is instead based on direct emission of electrons into the aqueous reactants.

Figure 1 shows an energy level diagram for diamond[6,7] and some redox reactions of importance.[3,7,8] When the surface of diamond is terminated with H atoms its conduction band typically lies at -5.2 V versus SHE, thus placing it above the one-electron reduction potential of CO_2, and even higher than the energy of a free electron in space (the vacuum level).[9] When H-terminated diamond is illuminated with above-bandgap ($E_{gap} = 5.5$ eV or $\lambda < 225$ nm) light, absorption of light by the diamond (1) excites electrons to the conduction band. These electrons are readily ejected into the adjacent aqueous phase (2), where they quickly relax (3) to form solvated electrons[6,10] and other high-energy species.

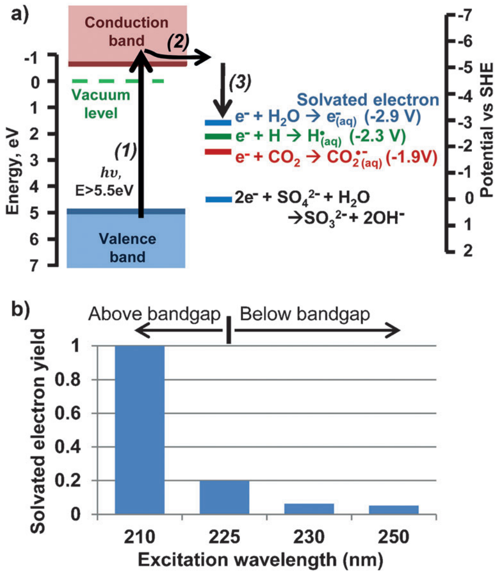

Figure 1. a) Energy diagram of H-terminated diamond compared with relevant redox potentials on absolute energy scale (left) and electrochemical energy scale (right).[8,11] E^0 values are shown for production of solvated electron ($e^-_{(aq)}$), hydrogen atom ($H^\bullet$) and CO_2 radical anion ($CO_2^{\bullet -}$). ($E(SO_4^{2-}/SO_3^{2-})$ for counter-electrode is shown for pH 3.2. b) Solvated-electron yield versus wavelength from transient absorption measurements, normalized to yield at 210 nm.

We can directly observe solvated electrons by measuring the transient absorption of a $\lambda = 705$ nm laser beam grazing a diamond surface, which is then exposed to a brief pulse of ultraviolet light, as described in the Supporting Information. Figure 1b shows measurements of the solvated electron yield relative to the value at $\lambda = 210$ nm. These data show that the electron yield is much greater using above-bandgap excitation ($\lambda < 225$ nm) than that at longer wavelengths, thus confirming that absorption of light in the bulk diamond and subsequent electron emission from the diamond conduction band is more

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efficient at creating solvated electrons compared with other possible sub-bandgap excitation processes.

To establish how these solvated electrons induce reduction of CO_2 into CO, we conducted experiments using inexpensive "electrochemical grade" boron-doped diamond (BDD) substrates (Element Six, Inc., resistivity $< 0.05\,\text{ohm}\,\text{cm}^{-1}$) supported within a two-compartment quartz electrochemical cell. As shown previously,[6] the use of conductive, boron-doped diamond facilitates electron emission by allowing diamond to act as the electron emitter, while a platinum counter electrode can be used to perform an oxidation reaction to maintain charge neutrality. The experimental apparatus and procedures are described in the Supporting Information. Briefly, the diamond sample in a Na_2SO_4 supporting electrolyte is connected to a platinum counter electrode immersed in a Na_2SO_4/Na_2SO_3 solution. Sulfite acts as a sacrificial hole scavenger by the oxidation half-reaction $SO_3^{2-} + 2\,OH^- \rightarrow SO_4^{2-} + H_2O + 2\,e^-$, ($E = -0.27$ V under reaction conditions). The quartz cell is housed within a reactor (Parr, Inc.) with a fused silica window, pressurized to 2.5 MPa (~25 times atmospheric pressure) with CO_2, and the diamond sample is illuminated with broadband light from a HgXe lamp. Under these reaction conditions the pH is about 3.2.[12] After reaction the gas-phase headspace is released into a gas cell and analyzed using Fourier-transform infrared spectroscopy (FTIR). The liquid is analyzed using ion chromatography (IC), gas chromatography mass spectroscopy (GC-MS), and nuclear magnetic resonance (NMR) spectroscopy.

Figure 2 shows FTIR spectra of the gas-phase headspace after CO_2 photoreduction by illumination of a diamond sample. The spectrum from illuminated diamond in CO_2/water shows distinct absorption lines of CO. The features shown here are the P($\Delta J = -1$) and R($\Delta J = +1$) rotational branches associated with excitation from the lowest ($v = 0$) to the first excited ($v = 1$) vibrational state of CO. No significant CO is produced in the absence of UV light (Figure 2; No illumination) or in an argon-purged solution (Figure 2; No CO_2). A very small amount of CO is observed when a CO_2-saturated solution is illuminated without the diamond sample (Figure 2; No diamond). This CO arises because CO_2 has a very small photochemical reactivity at short wavelengths.[13] All features in Figure 2 arise from CO and CO_2. The positions and intensities are reproduced almost exactly using known spectral constants (see the Supporting Information).[14]

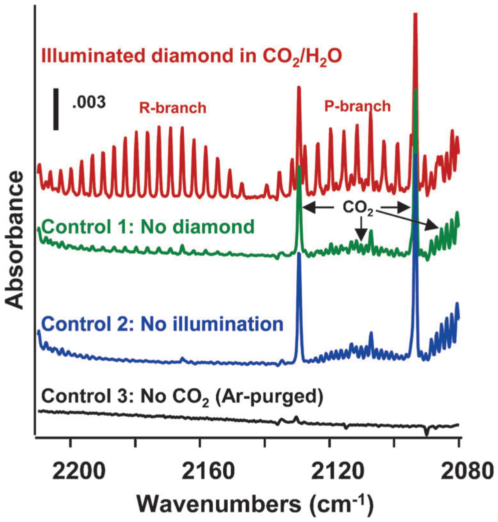

Figure 2. FTIR spectra of gaseous headspace demonstrating reduction of CO_2 to CO by illuminated diamond, along with control samples.

We calibrated our apparatus to establish the absolute CO yield and determined that a 1 cm^2 diamond sample typically produces about 300 μg of CO, thus corresponding to a concentration of CO in the gas phase of about 100 parts per million (ppm). We attempted to detect H_2 by GC and found that the concentration of H_2 product lies below our detection limit of 5 ppm. This result demonstrates that reduction of H^+ to H_2 does not compete with reduction of CO_2 into CO. IC measurements of the liquid phase revealed only a small amount (28 μg) of the formate ion. We also attempted to detect other liquid-phase products using both GC-MS and NMR methods, but the amounts were below the detection limit of less than 1 $\text{mg}\,\text{L}^{-1}$ (corresponding to a ca. 80 μg of product). Our results indicate that the reduction of CO_2 occurs with high selectivity for CO, and also with high (> 95 %) selectivity for CO_2 reduction over proton reduction.

We evaluated whether the CO produced arose entirely from excitation across the diamond bandgap or whether sub-bandgap could induce CO_2 reduction, by comparing the CO production using broad-spectrum light with CO production when a $\lambda = 225$ nm cutoff filter was inserted (thereby passing only sub-bandgap light). This experiment (see the Supporting Information) showed that no CO was produced using excitation wavelengths greater than $\lambda = 225$ nm. This result is consistent with the solvated electron yield results of Figure 1 b.

To maintain charge neutrality, every electron emitted from the diamond must be accompanied by an oxidation reaction of the valence-band holes. In a previous study using identical samples[6] we found that the valence-band edge lies at +0.3 V versus SHE[15] (Figure 1), and is in agreement with earlier studies.[7] The oxidation of diamond by $C + H_2O \rightarrow CO + 2\,H^+ + 2\,e^-$ has an associated reduction potential of $E_{\text{red}} = 0.71$ V at pH 3.2 and should therefore not occur.[16] To prove that our CO product comes from CO_2 and not from the diamond substrate or other sources, we used isotopically labeled $^{13}CO_2$ as the source to perform the reaction. Figure 3 shows FTIR spectra of the gas-phase products starting from natural-abundance CO_2 (which we refer to as $^{12}CO_2$) and starting from $^{13}CO_2$. Also shown are simulations showing the spectra expected from pure ^{12}CO and ^{13}CO based on the HITRAN database.[14] The experimental FTIR spectra show clear rotational-vibrational lines expected for isotopically pure products and exactly match the simulated spectra. Using $^{12}CO_2$ yields the ^{12}CO product with its band center near 2140 cm^{-1}, and using $^{13}CO_2$ produces shifted bands centered near 2100 cm^{-1} for ^{13}CO. In each case the shifted spikes and pattern between 2100 cm^{-1} and 2000 cm^{-1} are from CO_2 (also simulated in the Supporting Information). These isotope data prove that the CO product arises from the photoreduction of

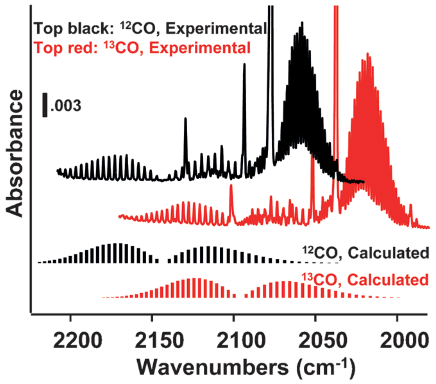

Figure 3. FTIR spectra showing CO produced from diamond illuminated in contact with isotopically labeled CO_2. The data show that ^{13}CO and ^{12}CO are produced from $^{13}CO_2$ and $^{12}CO_2$ starting materials, respectively. Also shown are calculated spectra for ^{13}CO and ^{12}CO.

CO_2 introduced as a gas-phase reactant and not from diamond or other sources.

The iodide ion (I^-) is also known to generate solvated electrons upon UV exposure.[17] As a comparison, we placed a 10 mM KI solution into the pressure vessel, pressurized with CO_2 to 2.5 MPa, and exposed the sample to UV light for 16 hours. Figure S8 in the Supporting Information shows FTIR spectra of the resulting gas-phase headspace. Again CO is the major product with very little formation of H_2.

Despite much effort, the mechanistic pathways for photochemical CO_2 reduction remain only partially understood.[1,18] Nearly all prior photochemical studies have focused on PCET reactions such as $CO_2 + 2H^+ + 2e^- \rightarrow CO + H_2O$.[1] However, PCET reactions require adsorption of both CO_2 and H^+ and multi-electron transfers, thus leading to complex pathways and multiple products, including H_2.[2a,b,18a,b,19] The high selectivity we observe with almost no H_2 suggests the solvated electron-induced reduction of CO_2 occurs by a unique pathway.

A notable difference between our work and all previous work on electrocatalytic and photocatalytic reduction of CO_2 is that the diamond electrode introduces electrons directly into the aqueous phase and it is therefore unnecessary (even undesirable) for reactants, intermediates, or products to bind to the surface. Instead, once the electrons are emitted, subsequent reactions occur in homogeneous solution. As depicted in Figure 1, electrons emitted from the diamond conduction band into water could react directly with CO_2 to form $CO_2^{\bullet-}$ in free solution (not adsorbed on a surface) or could relax first and produce solvated electrons $e^-_{(aq)}$. These then react with CO_2 to form $CO_2^{\bullet-}$ or with H^+ to form neutral hydrogen atoms ($H^\bullet$). The reaction $e^-_{(aq)} + CO_2 \rightarrow CO_2^{\bullet-}$ has a rate constant of $k = 7.7\times10^9\,\text{M}^{-1}\text{s}^{-1}$, while the competing reaction with protons $e^-_{(aq)} + H^+ \rightarrow H^\bullet$ has a rate constant of $k = 2.3\times10^{10}\,\text{M}^{-1}\text{s}^{-1}$.[20] At a CO_2 pressure of 2.5 MPa and a temperature of 300 K, $[CO_{2(aq)}] = 0.8\,\text{M}$[21] and the pH is 3.2.[12] Since $[CO_{2(aq)}](0.8\,\text{M}) \gg [H^+](8\times10^{-4}\,\text{M})$, the vast majority of solvated electrons react by $e^-_{(aq)} + CO_2 \rightarrow CO_2^{\bullet-}$. These rate equations predict that $[H^\bullet]$ will be small and that solvated electrons predominantly react with CO_2 to form $CO_2^{\bullet-}$. Since $CO_2^{\bullet-}$ is approximately 0.4 eV lower in energy than $[H^\bullet]$ (see Figure 1), $H^\bullet$ atoms never accumulate and therefore the bimolecular reaction $H^\bullet + H^\bullet \rightarrow H_2$ (an undesirable side-reaction) is unimportant. Our observation of high selectivity for CO reduction over proton reduction with no detectable H_2 product strongly supports this model and highlights the importance of $CO_2^{\bullet-}$ as a reservoir for electrons.

Electrochemical studies have hypothesized that the one-electron reduction of surface-adsorbed CO_2 to form adsorbed $CO_2^{\bullet-}{}_{(ads)}$ might occur at high overpotentials and then undergo additional bimolecular coupling or proton-coupled electron-transfer reactions to form CO and formate.[2b,e,18a,c,d,22] Hori et al.[18a] hypothesized that protonation of $CO_2^{\bullet-}{}_{(ads)}$ could form adsorbed HOCO and then be reduced to OH + CO. Saveant et al.[18c,22] proposed that two $CO_2^{\bullet-}{}_{(ads)}$ anions could form a transient intermediate which disproportionates by $2CO_2^{\bullet-} \rightarrow CO + CO_3^{2-}$ in a solution with low proton concentrations.[22] On a surface, pathways involving bimolecular coupling are important because of the locally high concentrations of accumulated species, but such reactions are less likely to occur in homogeneous solution. However, $CO_2^{\bullet-}$ in large water clusters photodissociates into CO and O^- when illuminated with light at $\lambda = 266$ nm or $\lambda = 355$ nm.[23] This result suggests that CO production in our studies may involve initial formation of $CO_2^{\bullet-}$ and subsequent photodissociation of $CO_2^{\bullet-}$ to produce the final CO product. To ensure that our CO product did not come from photodissociation of formate (a common CO_2 reduction product),[18a] we tested the photochemical activity of formate-containing solutions. These experiments yielded very little CO (see Figure S9 in the Supporting Information), thus showing that CO comes from the $CO_2^{\bullet-}$ intermediate.

While further studies will undoubtedly be needed to fully resolve the detailed mechanistic pathways, our results demonstrate that CO_2 can be efficiently and selectively reduced to CO using solvated electrons. The unique electronic structure of H-terminated diamond allows it to be used as a convenient solid-state source of electrons at the conduction-band energy. The high energy of these electrons enables formation of solvated electrons and the direct one-electron reduction of CO_2 to $CO_2^{\bullet-}$ in solution, a reaction step not accessible with other water-stable semiconductor photocatalysts. The rapid reaction of solvated electrons with CO_2 at 2.5 MPa allows CO_2 reduction to outcompete proton reduction even at pH 3.2, thus resulting in selective reduction of CO_2 with only minimal production of H_2 as a side product. This work represents a new approach to catalysis by bringing electrons as a reagent directly into reactant solutions, thus enabling new mechanistic pathways which can provide unique and selective product distributions.

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