

# CO<sub>2</sub> Reduction to Higher Hydrocarbons by Plasma Discharge in Carbonated Water

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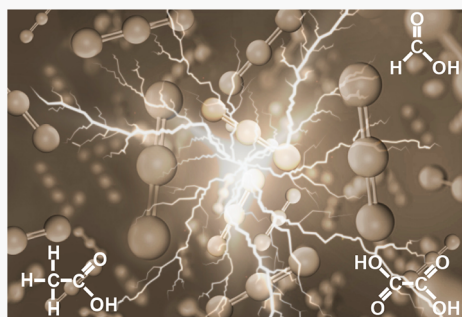


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Supporting Information

**ABSTRACT:** By discharging nanosecond high-voltage pulses in CO<sub>2</sub>-saturated water, we observe CO<sub>2</sub> reduction to higher-order hydrocarbons, including acetic acid, formic acid, and oxalate. Here, the plasma emission spectra exhibit Swan bands, which correspond to C<sub>2</sub> species, indicating that in addition to reducing CO<sub>2</sub>, C<sub>2</sub>-species are formed, which presents the possibility of converting a notorious greenhouse gas into liquid (*i.e.*, dense) hydrocarbon fuels. In order to characterize various hydrocarbon products formed in this process, cryogenic NMR spectroscopy and liquid ion chromatography are performed *ex situ*. Here, we observe clear peaks corresponding to formic acid (CH<sub>2</sub>O<sub>2</sub>) and acetic acid (CH<sub>3</sub>COOH). We have also observed the presence of formate (HCO<sub>2</sub><sup>−</sup>), acetate (C<sub>2</sub>H<sub>3</sub>O<sub>2</sub><sup>−</sup>), and oxalate (C<sub>2</sub>O<sub>4</sub><sup>2−</sup>) using liquid ion chromatography. Plasma emission spectroscopy exhibits spectral signatures associated with atomic hydrogen and atomic oxygen due to the plasma discharge in water, which facilitate (and compete with) the CO<sub>2</sub>-to-hydrocarbon conversion.



With increasing levels of greenhouse gases in our atmosphere, CO<sub>2</sub> reduction processes are of broad interest because of their ability to mitigate global warming. Many research groups (including our own) have focused on electrochemical and photoelectrochemical CO<sub>2</sub> reduction, involving various metal electrodes, molecule catalysts, and plasmon-enhanced approaches.<sup>1–15</sup> The reduction of CO<sub>2</sub> with H<sub>2</sub>O to various hydrocarbons is a complex reaction system requiring up to 8 electrons and many intermediate species, some of which have extremely high energy barriers. The mechanism for electrochemical CO<sub>2</sub> reduction was first proposed by Bockris *et al.*<sup>16–18</sup> The high overpotential required for this reaction was attributed to the formation of the (CO<sub>2</sub>)<sup>−</sup> intermediate, CO<sub>2</sub> + e<sup>−</sup> → (CO<sub>2</sub>)<sup>−</sup>, which is the rate-limiting step of CO<sub>2</sub> reduction. The highly energetic species provided by the plasma (*i.e.*, nonequilibrium approach) provide a strategy for overcoming the reaction barrier associated with the (CO<sub>2</sub>)<sup>−</sup> reaction intermediate. Dielectric barrier discharge has been reported for conversion of carbon dioxide to syngas and hydrocarbons at atmosphere pressure with or without catalyst.<sup>19–21</sup> Heijkers *et al.*, Masaharu *et al.*, and Mitsingas *et al.* reported the decomposition of CO<sub>2</sub> by microwave plasma in carrier gases of N<sub>2</sub>, Ar, or He.<sup>22–24</sup> Pulsed plasmas have also been used to drive gas-phase CO<sub>2</sub> reduction reactions and subsequent conversion to hydrocarbon fuels (syngas).<sup>25–28</sup>

While there have been many papers reporting CO<sub>2</sub> reduction to higher-order hydrocarbons in the gas phase,<sup>29–35</sup> to our knowledge few have shown CO<sub>2</sub> reduction in carbonated water by plasma discharge. Rumbach *et al.* showed that CO<sub>2</sub> can be reduced in an aqueous medium using a plasma-based electrode to produce oxalate and formate.<sup>36</sup> In their work, the plasma discharge was generated in the gas phase (above liquid) and highly energetic electrons were injected into the solution, thus producing solvated electrons. Generating a plasma discharge in aqueous solutions requires voltages significantly higher than that in the gas phase because of the relatively high dielectric strength of the aqueous medium. Common approaches to lowering the discharge threshold include using a needle electrode, a gas diffuser, or pressurization to create bubbles, enabling the discharge to be initiated within a small bubble on the electrode surface and then propagate into the aqueous phase.<sup>37–45</sup>

In the work presented here, we demonstrate CO<sub>2</sub> reduction to higher-order hydrocarbons by discharging a nanosecond pulsed plasma in carbonated (*i.e.*, CO<sub>2</sub>-saturated) aqueous

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solution. Here, the carbonated water gives rise to small bubbles which lower the voltage needed to generate the plasma and also provides a relatively high concentration of  $\text{CO}_2$  in the aqueous solution.

In the work presented here, the transient pulsed plasma is produced on a glass slide-based reactor with a high-voltage pulse generator (Model 30X, Transient Plasma Systems, Inc.), which produces pulses with peak voltages up to 30 kV, pulse rise times of 5–10 ns, and repetition rates up to 2 kHz. A typical waveform is shown in Figure 1b. Figure S1 in the

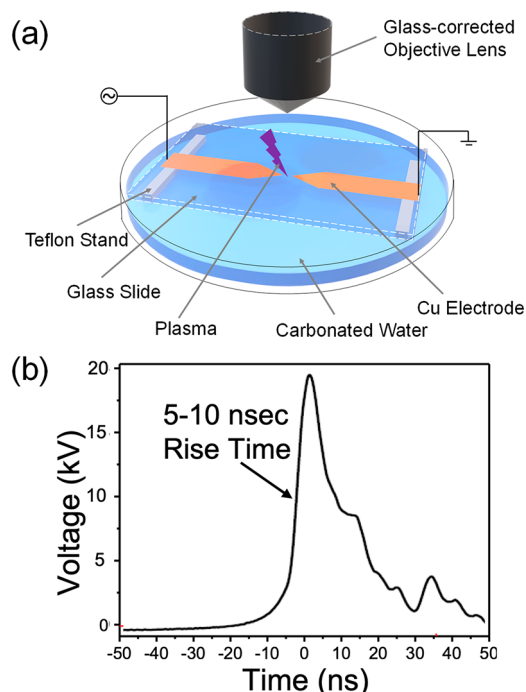


Figure 1. (a) Schematic diagram of the experimental setup used to take *in situ* plasma emission spectra. (b) Typical output characteristics of nanosecond high-voltage pulse generator.

Supporting Information shows a plot of our waveform characteristics over several cycles, in which the short nanosecond pulses are repeated at a rate of 1 kHz, giving rise to a duty cycle of approximately  $1:10^5$ . The *in situ* plasma emission spectra are taken with an *inVia* Raman microspectrometer (Renishaw, Inc.). The cryogenic NMR spectroscopy and liquid ion chromatography (Dionex, ICS-2000) are performed *ex situ* before and after 30 min plasma discharges in 10 mL of carbonated solution. The Dionex Ion Chromatography System (ICS-2000, Thermo Fisher Scientific, Sunnyvale, CA) is equipped with a refrigerated autosampler and has a detection limit of 0.1 mg/L for the tested compounds.

Figure 1a shows a schematic diagram of our experimental setup for observing plasma emission spectroscopy. Here, two copper tape electrodes, separated by a 5 mm gap, are attached to the bottom side of a 1 mm-thick glass slide, and immersed in the carbonated water electrolyte, while the top surface of the glass slide remains in air. This geometry enables plasma emission spectra to be taken efficiently using a glass-corrected objective lens. Figure 2 shows several photographs of the plasma discharge using copper tape electrodes deposited on a glass slide in DI water (deionized water) and  $\text{CO}_2$ -saturated DI water at 13 kV (Figure 2a) and 28 kV (Figure 2b). In DI water, 28 kV pulses are needed in order to generate a plasma, which is much higher than the voltages required to create a plasma in the gas phase ( $\sim 5$  kV)<sup>46,47</sup> because of the relatively high dielectric strength of the aqueous medium, which has a breakdown field 5–6 times higher than that of air. The copper electrodes are patterned with sharp tips to provide additional field enhancement to help initiate the plasma. In carbonated water, we can achieve plasma discharge at 13 kV because of the presence of bubbles. The aqueous solution can potentially provide a higher density of reactants than gas-phase reactions. In our measurement, the carbonated water was produced at room temperature (25 °C) using a SodaStream water-carbonator, which is capable of carbonating the water at approximately 20 PSI, from which we estimate the initial amount of  $\text{CO}_2$  in solution to be around 2 g/L.<sup>48</sup> Carbon dioxide dissolves in water at 0.2–1.0% concentration (1.45–3.0 g/L), which creates carbonic acid ( $\text{H}_2\text{CO}_3$ ).<sup>49–52</sup> However,

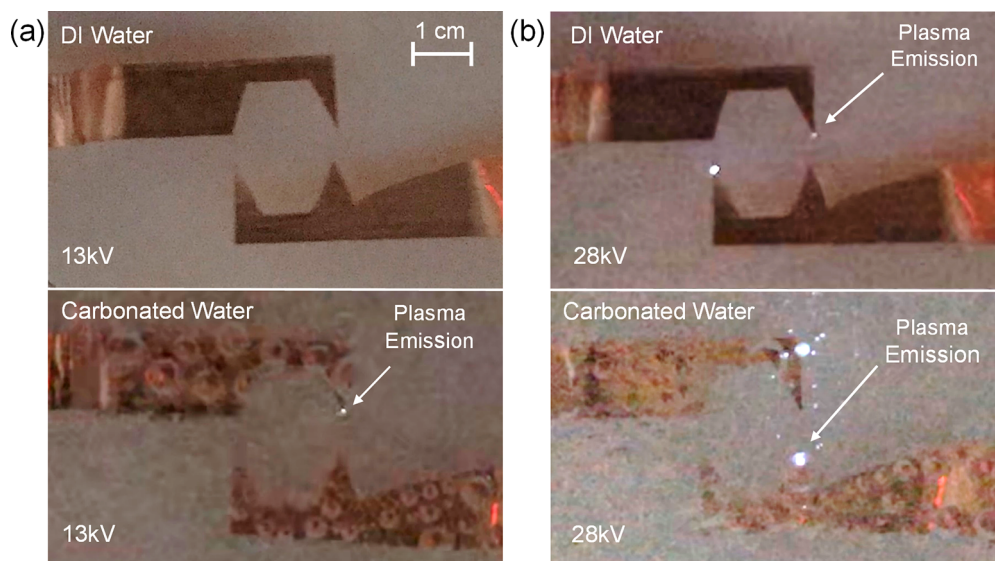


Figure 2. Plasma emission generated with copper tape electrodes in deionized (DI) water and carbonated water at (a) 13 kV and (b) 28 kV.

the plasma discharge is likely initiated within bubbles of gaseous  $\text{CO}_2$ , because it is easier to achieve a plasma discharge in gas than in liquid. That is, the reported dielectric strength of air is  $22\times$  less than that of water. We believe that it is these  $\text{CO}_2$ -rich pockets that enable  $\text{C}_2$  formation, in the gas-phase plasma, liquid phase, or some interaction between the gas and liquid phases.<sup>24,53–57</sup>

Figure 3 shows plasma emission spectra of our transient pulsed plasma obtained in a  $\text{CO}_2$ -saturated aqueous environ-

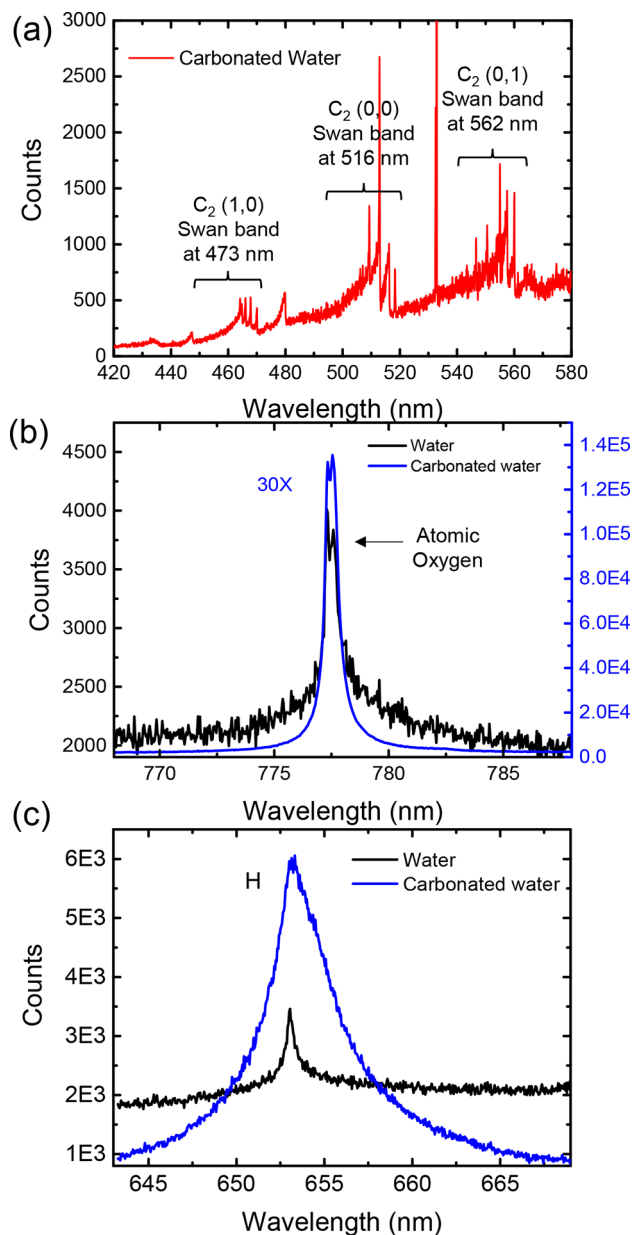


Figure 3. Plasma emission spectra of (a)  $\text{C}_2$  species, (b) atomic O, and (c) H radicals observed in DI water and carbonated water with 15 kV pulses at the repetition rate of 400 Hz.

ment taken with a high numerical aperture objective lens, as illustrated in Figure 1a. Here, we observe several sets of Swan bands, which correspond to  $\text{C}_2$  (diatomic carbon) species.<sup>58,59</sup> For example,  $\text{C}_2(1,0)$ ,  $\text{C}_2(0,0)$ , and  $\text{C}_2(0,1)$  correspond to different vibrational and rotational states of this diatomic species. This indicates that, in addition to reducing  $\text{CO}_2$  (*i.e.*, a

high barrier reaction),  $\text{C}_2$ -species are formed, which may subsequently convert to acetate ( $\text{C}_2\text{H}_3\text{O}_2^-$ ) and oxalate ( $\text{C}_2\text{O}_4^{2-}$ ), as detected by liquid ion chromatography (see Figure 4). While copper is a well-known  $\text{CO}_2$  electro-

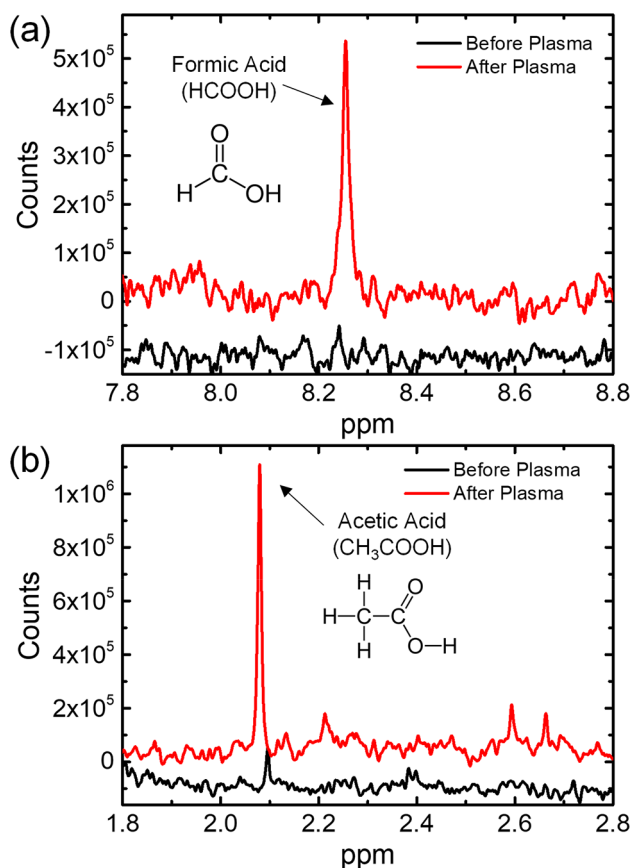


Figure 4. Cryogenic  $^1\text{H}$  NMR spectra taken before and after 30 min plasma discharge in  $\text{CO}_2$ -saturated water of (a) formic acid and (b) acetic acid.

catalyst,<sup>1,6,60–63</sup> we have conducted additional experiments with aluminum electrodes instead of copper. Here, we found comparable  $\text{C}_2$  species as plotted in the spectra shown in Figure S2. Therefore, we do not believe that the copper electrodes themselves are catalytically activating the  $\text{CO}_2$  independent of the plasma.

From a pulsed discharge in water, we also observe features in the emission spectra associated with the H and O radicals, which correspond to highly chemically reactive species.<sup>64–68</sup> One of the main challenges in producing hydrocarbons using a plasma is that the atomic oxygen rapidly drives the back reaction of carbon to CO and  $\text{CO}_2$ . Panels b and c of Figure 3 show the plasma emission spectra corresponding to atomic oxygen and hydrogen. Here, both the H and O radicals are more easily generated in carbonated water than in DI water because of the presence of bubbles which assist in the plasma discharge process, thereby generating a higher-density plasma under the same voltage conditions. As mentioned above, the formation of  $\text{CO}_2$  bubbles gives rise to a lower threshold for plasma discharge than in DI water. This finding is consistent with previous papers on plasma discharge in water, most of which provide some strategy for creating bubbles and thus lowering the plasma discharge threshold.<sup>37–45</sup> Dobrynin and co-workers investigated the initiation stage of nanosecond



breakdown in liquid, which revealed the appearance of discontinuities in the liquid (cavitation) under the influence of electrostriction forces.<sup>69</sup> It is possible that this cavitation effect is more pronounced in the carbonated water electrolyte; however, these experiments could not be performed with our existing experimental setup.

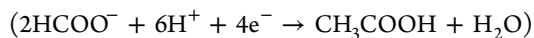
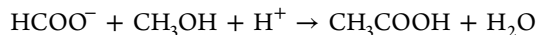
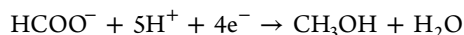
In order to quantify the hydrocarbons produced by the plasma discharge in carbonated water, we performed cryogenic NMR spectroscopy of various products in water (*i.e.*, hydrocarbons) and liquid ion chromatography *ex situ*. Figure 4 shows cryogenic NMR spectra taken before and after plasma discharge in CO<sub>2</sub>-saturated water. Here, we observe clear peaks corresponding to formic acid and acetic acid, which corresponds to a C<sub>2</sub>-hydrocarbon species. We have also observed the presence of oxalates (*i.e.*, C<sub>2</sub>O<sub>4</sub><sup>2-</sup>) using liquid ion chromatography, as shown in Figure S4, which also correspond to C<sub>2</sub> species.

One possible reaction pathway takes place *via* hot electrons generated in the bubbles, which are subsequently injected into the aqueous solution forming solvated electrons, which have an extremely high reduction potential.<sup>70,71</sup> This reaction can potentially follow the pathway CO<sub>2</sub> + e<sup>-</sup> → CO<sub>2</sub><sup>-</sup> and then CO<sub>2</sub><sup>-</sup> + CO<sub>2</sub><sup>-</sup> → (CO<sub>2</sub><sup>-</sup>)<sub>2</sub> for oxalate and CO<sub>2</sub><sup>-</sup> + H<sup>+</sup> + e<sup>-</sup> → HCOO<sup>-</sup> for formate.<sup>36,72–75</sup> Mota-Lima reported a theoretical overview of plasma/liquid interface as a platform for highly efficient CO<sub>2</sub> electroreduction to oxalate, in which the carboxyl radical anion (CO<sub>2</sub><sup>-</sup>(aq)) plays an important role.<sup>75</sup> Here, the one-electron reduction to CO<sub>2</sub><sup>-</sup> represents a high-barrier intermediate that is enabled by the high-energy electrons in the plasma and subsequent generation of solvated electrons.<sup>36</sup> This is essentially homogeneous chemistry in the aqueous phase driven by solvated electrons, which have an extremely low (*i.e.*, strongly) reducing potential (−2.87 V vs SHE or only 1.41 eV below vacuum). These solvated electrons, while difficult to form, have been used to drive difficult reactions such as ammonia formation, which transforms N<sub>2</sub> and water to NH<sub>3</sub> without a catalyst surface, as well as CO<sub>2</sub> reduction to CO.<sup>70,71,76,77</sup>

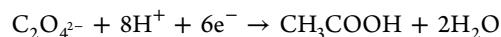
While it is possible that CO<sub>2</sub> reduction is induced by the formation of solvated electrons reported previously by Rumbach *et al.*,<sup>36,71</sup> the lifetime and penetration depth of these solvated electrons are quite small. It is, therefore, more likely that the reaction occurs in the gas phase (*i.e.*, in the bubbles),<sup>25–28</sup> where the CO<sub>2</sub> in the liquid phase continuously supplements the gas phase to ensure the continued progress of the reaction. The gas-phase reaction (in the bubble) can involve only CO<sub>2</sub>, H radicals, O radicals, and H<sub>2</sub>O. We have detected H<sub>2</sub> and CO by GC measurements (see Figure S3), which could serve as possible reaction intermediates. In this case, this process involves mixed phases: liquid, gas, and plasma. However, further studies would be needed in order to establish the precise proportion of these reactions that occur in the liquid and gas phases.

The production of acetic acid is especially interesting, as it has not been observed before and likely has a more complex reaction pathway than either formate or oxalate. While a detailed pathway for this reaction is not currently understood, two possible reaction pathways for acetic acid include the following:

### (1) *Via formate*



### (2) *Via oxalate*



Another possible mechanism was reported by Genovese *et al.* for C–C bond formation in the electrocatalytic reduction of CO<sub>2</sub> to acetic acid *via* the reaction of CO<sub>2</sub><sup>-</sup> with surface adsorbed −CH<sub>3</sub> species.<sup>78</sup>

In this work, the formic acid and acetic acid yields are estimated to be 2.2 × 10<sup>−3</sup> and 4.4 × 10<sup>−4</sup> mol/L, respectively, based on cryogenic <sup>1</sup>H NMR spectroscopy with respect to a known amount of methanol (CH<sub>3</sub>OH). The voltage and current waveforms (vs time) are plotted in Figure S6, which indicate an energy per pulse of 18.6 mJ. While the plasma density depends on many factors, including electrode geometry and dielectric medium, we estimate the efficiency of formic acid and acetic acid production to be 1.6 × 10<sup>−9</sup> moles and 3.3 × 10<sup>−10</sup> moles per Joule of energy based on the energy per pulse multiplied by the pulse repetition rate. While previous work on plasma-based CO<sub>2</sub> conversion carried out in the gas is typically reported in % CO<sub>2</sub> conversion efficiencies (*e.g.*, 5–35% energy efficiencies<sup>31,79</sup> or 10% faradaic efficiency<sup>36</sup>), no values in mol/Joule have been put forth for plasma discharge in an aqueous electrolyte. Assuming the formic acid and acetic acid production proceed in the gas phase, on the basis of the reaction enthalpy of the overall reactions CO<sub>2</sub> + H<sub>2</sub>O → HCOOH + 1/2 O<sub>2</sub> (ΔH = 243 kJ/mol) and 2CO<sub>2</sub> + 2H<sub>2</sub>O → CH<sub>3</sub>COOH + 2O<sub>2</sub> (ΔH = 875 kJ/mol), we can estimate their energy efficiency to be around 1 × 10<sup>−7</sup> mol/J for formic acid and 1 × 10<sup>−8</sup> mol/J for acetic acid, which is 2 orders of magnitude larger than our results.

It should be noted that our current approach is far from optimized, and we believe several orders of magnitude improvement can be achieved by improving the electrode geometry, introducing catalytically active surfaces, and controlling the local electrode environment/potential. While discharging a plasma in water is particularly difficult, this provides a unique environment in which the ion concentrations can be varied by 14 orders of magnitude (*e.g.*, pH 0–14) (unlike gas-phase reactions), ultimately enabling us to better control reaction rates and selectivity. Upon introducing a catalytically active surface (*e.g.*, NiO), this CO<sub>2</sub> reduction reaction can be driven more efficiently.<sup>34,35</sup> It is interesting to note that the C<sub>2</sub> swan bands presented in Figure S2 are roughly a factor or 2 less intense than those obtained with Cu, plotted in Figure 3a. However, because of the inherent fluctuations in this water-based discharge, it is very hard to compare intensities. Lastly, by implementing electrode geometries that provide electric field enhancement, significant improvements in the overall efficiency can be achieved. For example, the active area over which the plasma is discharged in this work is limited to several square micrometers. Using a transmission line geometry, much larger areas of approximately square millimeters can be achieved.<sup>80–83</sup> Further approaches to improving efficiency include employing an active means of

separating the products from the reactants (e.g., azeotropic distillation), which enable the accumulation of a significant amount of product while minimizing destructive back reactions.

We have demonstrated CO<sub>2</sub> reduction to C<sub>1</sub> and C<sub>2</sub> hydrocarbons by discharging nanosecond high-voltage pulses in carbonated (i.e., CO<sub>2</sub>-saturated) water. After discharging plasma, we observe the formation of acetic acid, formic acid, and oxalate through the complex interaction between liquid, gas, and plasma phases. Swan bands are exhibited in the plasma emission spectra, confirming the formation of C<sub>2</sub> (diatomic carbon radical) species. A substantially lower threshold voltage is needed to generate a plasma in carbonated water than in DI water because of bubbles formed on the electrode surface. Cryogenic NMR spectroscopy reveals clear peaks corresponding to formic acid (CH<sub>2</sub>O<sub>2</sub>) and acetic acid (CH<sub>3</sub>COOH), and liquid ion chromatography shows the presence of oxalates (i.e., C<sub>2</sub>O<sub>4</sub><sup>2-</sup>) after discharging plasma in carbonated water. Electrodes mounted on a glass slide form a submerged planar surface discharge that enables plasma emission spectra to be obtained *in situ*, which show spectral signatures of atomic hydrogen and atomic oxygen, representing intermediate species that facilitate (and compete with) the conversion of CO<sub>2</sub> to hydrocarbons.

## ■ ASSOCIATED CONTENT

### SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsenerylett.1c01666>.

V–I characteristic measurements, emission spectrum measurements, gas chromatography (GC) measurements, and liquid ion chromatography (LIC) measurements (PDF)

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## Notes

The authors declare no competing financial interest.

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