Plasmonic photosynthesis of C$_1$–C$_3$ hydrocarbons from carbon dioxide assisted by an ionic liquid

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Photochemical conversion of CO$_2$ into fuels has promise as a strategy for storage of intermittent solar energy in the form of chemical bonds. However, higher-energy-value hydrocarbons are rarely produced by this strategy, because of kinetic challenges. Here we demonstrate a strategy for green-light-driven synthesis of C$_1$–C$_3$ hydrocarbons from CO$_2$ and H$_2$O. In this approach, plasmonic excitation of Au nanoparticles produces a charge-rich environment at the nanoparticle/solution interface conducive for CO$_2$ activation, while an ionic liquid stabilizes charged intermediates formed at this interface, facilitating multi-step reduction and C–C coupling. Methane, ethylene, acetylene, propane, and propene are photosynthesized with a C$_2^+$ selectivity of ~50% under the most optimal conditions. Hydrocarbon turnover exhibits a volcano relationship as a function of the ionic liquid concentration, the kinetic analysis of which coupled with density functional theory simulations provides mechanistic insights into the synergy between plasmonic excitation and the ionic liquid.
Carbon dioxide (CO$_2$) fixation is recognized to be a much-needed component of a carbon-neutral energy strategy\cite{1,2}. Although CO$_2$ is relatively unreactive, various catalytic processes triggered by heat (thermochemical)\cite{3,4}, electricity (electrochemical)\cite{5,6,7,8,9,10,11,12,13,14}, and light (photochemical)\cite{15,16,17,18,19,20,21,22,23,24,25,26} are being explored for activating CO$_2$ and recycling it back to valuable petrochemicals. Sunlight-driven conversion of CO$_2$ to fuels is particularly attractive as a means to store intermittent solar energy in the form of C-C and C-H bonds. Semiconductor and metal-catalyzed photoelectrolytic reduction of CO$_2$ has shown promise; however, these processes have often required ultraviolet (UV) light and/or considerable electrical energy input, or they do not favor energy-rich hydrocarbon products. Longer-chain hydrocarbons possess higher energy densities. Moreover, hydrocarbons in the liquid state are easier to transport\textsuperscript{29,30}. However, the formation of longer-chain hydrocarbons from CO$_2$ requires multiple electron ($e^-$) and proton (H$^+$) transfer steps, as well as C-C bond formation\textsuperscript{31,32}, which pose major kinetic bottlenecks.

Here we demonstrate a visible-light-driven route for the conversion of CO$_2$ and H$_2$O into C$_1$–C$_3$ hydrocarbons. The scheme does not involve the application of an electrochemical potential, UV light, high temperatures, hydrogen gas, or a sacrificial agent. It uses green light as the sole energy input and driving agent. The strategy employs plasmonic Au nanoparticles (NPs) of a pseudospherical shape and an average diameter of ~12 nm, as characterized previously\textsuperscript{33}. Au NPs are known from electrochemical studies\textsuperscript{33} to activate CO$_2$. The choice of Au NPs was further driven by the relative chemical stability of Au against bulk oxidation and photoroscorrosion; the other two common plasmonic metals, Ag and Cu, while electrocatalytically active for CO$_2$ reduction, are prone to oxidation in air, water, and/or light excitation. The Au NPs possess a strong localized surface plasmon resonance (LSPR) band centered around 520 nm (Fig. 1a), which enables strong, resonant absorption of green light. The LSPR excitation of the NPs yields energetic electron–hole ($e^-$–$h^+$) carriers via Landau damping. These $e^-$–$h^+$ carriers were shown in recent studies to drive redox conversions\textsuperscript{28,34,35}, especially the conversion of CO$_2$ to methane and ethane under blue–green light\textsuperscript{28}. However, in this past demonstration, isopropanol was used as a sacrificial $h^+$ scavenger to facilitate $e^-$–$h^+$ pair separation; otherwise, unproductive $e^-$–$h^+$ recombination dominated. Thus, isopropanol served as the $H^+$ source in this CO$_2$ reduction scheme, which posed a major limitation for net energy storage.

The present strategy overcomes this drawback and uses water as the $H^+$ source and does not require a sacrificial $h^+$ scavenger, thus constituting a truly fuel-forming reaction. The enhanced reactivity was enabled by the use of an ionic liquid (IL) medium, specifically comprised 1-ethyl-3-methylimidazolium tetrafluoroborate (EMIM-BF$_4$). Our choice was motivated by examples from electrolycatalytic CO$_2$ reduction reaction (CO$_2$RR) where the EMIM-BF$_4$ electrolyte, owing to its highly ionic character, stabilizes the high-energy CO$_2$$^\ast$ radical anion intermediate formed in the reaction and decreases the overpotential needed for CO$_2$RR\textsuperscript{37–42}. In addition, EMIM-BF$_4$ has a wide electrochemical window and high thermal stability\textsuperscript{43,44}. In our photocatalytic scheme, the EMIM-BF$_4$, as we find from kinetic analysis and density functional theory (DFT) simulations, promotes $e^-$ transfer at the interface of the photoexcited Au NP and adsorbed CO$_2$ (Fig. 1b), obviating the need for a $h^+$ scavenger or applied potential for $e^-$–$h^+$ separation.

Results
IL-mediated plasmonic CO$_2$ reduction. The photocatalyst had the form of a substrate-supported film of Au NPs immersed in an aqueous solution of EMIM-BF$_4$ saturated with CO$_2$ and contained inside a glass reactor (Supplementary Methods). The light excitation source comprised a continuous-wave (CW) laser of a wavelength of 532 nm light and an intensity of 1 W cm$^{-2}$. Under CW excitation, the steady-state temperature of the reaction medium got moderately elevated to ~48 °C. Hydrocarbon products collected in the reactor headspace were measured (Supplementary Figs. 1–11) using a gas chromatograph (GC) equipped with a flame ionization detector. The EMIM-BF$_4$ concentration was varied from 0 to 100 mol%, to find optimal conditions for CO$_2$RR. In 1–10 mol% EMIM-BF$_4$, the products of plasmon-excitation-driven CO$_2$RR were found to be C$_1$ (CH$_4$), C$_2$ (C$_2$H$_6$ and C$_3$H$_8$), and highly reduced C$_3$ (C$_3$H$_8$ and C$_3$H$_6$) hydrocarbons (Fig. 1c, d and Supplementary Note 1). This product profile is quite striking when one considers that the major product in electrochemical CO$_2$RR is carbon monoxide (CO) formed by 2e$^-$–2H$^+$ reduction of CO$_2$ (refs. 13–17). On the other hand, propane (C$_3$H$_8$), formed in our scheme, requires an overall 20e$^-$–20H$^+$ reduction and coupling of three CO$_2$ molecules. Such generation of C$_3$ hydrocarbons by artificial photosynthesis is challenging and therefore rare.

The CO$_2$RR activity depends on the IL concentration (Fig. 1c). In pure water the activity was nil, whereas in 1 mol% EMIM-BF$_4$ solution the generation of C$_1$, C$_2$, and C$_3$ hydrocarbons was observed. The CO$_2$RR activity, as quantified by turnover frequencies (TOFs) of the hydrocarbon products, increased dramatically with an increase in the EMIM-BF$_4$ concentration. The highest activity was found at 5 mol% EMIM-BF$_4$. Increasing the EMIM-BF$_4$ concentration further resulted in a sharp drop in the CO$_2$RR activity. In 100 mol% EMIM-BF$_4$ solution, the activity was nil, similar to that in pure water. Thus, the CO$_2$RR activity exhibits a volcano relationship as a function of the EMIM-BF$_4$ concentration (Fig. 1c). At all EMIM-BF$_4$ concentrations, where C$_1$, C$_2$, and C$_3$ hydrocarbons were produced, the product selectivity was found to follow the order: C$_1$ > C$_2$ > C$_3$. The selectivity for C$_2$+ production is ~50% in 1–10 mol% EMIM-BF$_4$ solution (Fig. 1d).

Non-hydrocarbon products were also characterized by a GC equipped with a thermal conductivity detector (TCD) (Supplementary Figs. 12–15). Considerable hydrogen (H$_2$) production was measured (Supplementary Fig. 12), the TOF of which was 138.2 NP$^{-1}$h$^{-1}$ in 5 mol% EMIM-BF$_4$ solution, the IL concentration where CO$_2$RR activity is the highest. The H$_2$ likely originates from the competing reduction of H$^+$ in the reaction medium (Supplementary Eq. (6)). In the GC-TCD measurements, there were no detection of CO (Supplementary Fig. 15), otherwise known to be a major product in electrocatalytic CO$_2$RR on Au (refs. 13–17). Of the possible oxidation products, there was no measurable production of O$_2$ (see Supplementary Information). H$_2$O$_2$ was detected (Supplementary Figs. 16–18) by the fluorogenic test employing a amplex red and horseradish peroxidase reagent\textsuperscript{45}. Thus, the oxidation of H$_2$O to H$_2$O$_2$ and H$_2$ (2H$_2$O $\rightarrow$ H$_2$O$_2$ + 2H$^+$ + 2e$^-$) is the likely oxidation half-reaction that consumes the photogenerated h$^+$. Control studies were performed, one without Au NPs, another without light, and a third without CO$_2$. The conditions were otherwise maintained the same as those in the photoreaction tests and a 5 mol% EMIM-BF$_4$ solution, found to be most optimal in the photoreaction tests, was employed. The control studies showed that the absence of any one of the components Au NPs, green light illumination, or CO$_2$ resulted in nil hydrogen production, despite the use of 5 mol% EMIM-BF$_4$ solution (Supplementary Fig. 19a–c). Thus, it is confirmed that the hydrocarbon production originates from green-light-driven CO$_2$ reduction on Au NPs. The control study without light excitation was performed at an elevated temperature of 50 °C so as to mimic
the steady-state bulk solution temperature of the reaction mixture in the photoreaction tests. The lack of CO2RR activity in this dark control study demonstrates that the CO2RR activity in the photoreaction tests does not originate from simply a photothermal effect of the light excitation. Rather a photoredox process facilitated by the Au NPs and the IL is responsible for the conversion of CO2 to hydrocarbons.

The plasmonic catalyst also exhibited stability and recyclability under the photoreaction conditions and IL media subjected on the catalyst. We tested the same substrate-supported Au NP film immersed in 5 mol% EMIM-BF4 over multiple cycles, each consisting of a 10 h photoreaction. The CO2RR activity and product selectivity, as determined from the TOFs of the hydrocarbon products, was maintained over the course of this multi-cycle test (Supplementary Fig. 20). As the NP film or EMIM-BF4 solution were not replenished between cycles, the maintenance of CO2RR activity over multiple cycles suggests that Au and EMIM-BF4 were not consumed, at any discernible levels, in the photoredox reaction.

The origin of products. Given the hydrocarbon profile of the product mixture, it was necessary to go beyond the control studies described above and confirm more directly that CO2, rather than carbon contamination or photolysis of the EMIM-BF4, was the source of the hydrocarbon products. For this confirmation, 13C isotope labeling was employed (Fig. 2 and Supplementary Figs. 21 and 22). In this labeling study, 13CO2 was employed as the reactant instead of 12CO2, whereas all other conditions were kept the same as those in other photoreaction tests. GC-mass spectrometry (GC-MS) was used for identification of the hydrocarbon products generated in the photoreaction (Fig. 2a). The GC-MS analysis confirmed the presence of 13CH4 (Fig. 2b) and 13C2H2 (Fig. 2c), manifested by their characteristic mass fragmentation patterns, shifted to higher m/z compared with reference fragmentation patterns of 12CH4 and 12C2H2, respectively. Thus, isotope labeling confirms CO2 to be the origin of hydrocarbon products.

The role of the IL. We attempted to gain a mechanistic understanding of this catalytic scheme focusing on the question of how the IL promotes CO2RR activity. It was observed that the presence of EMIM-BF4 in the aqueous medium results in a considerably acidic pH (Supplementary Fig. 23): the 5 mol% EMIM-BF4 solution has a pH of 2.95. To determine whether this acidity is responsible for the enhanced CO2RR activity in a EMIM-BF4 solution, we performed a photoreaction in deionized water containing no EMIM-BF4 but with a pH of 2.93 achieved using acid (Supplementary Fig. 19d). All other conditions were kept the same as in the photoreactions in EMIM-BF4 solutions. In this EMIM-BF4-free photoreaction, no products were observed, which demonstrated that the high acidity or H+ concentration, [H+], of
the EMIM-BF₄-containing medium is not the sole cause of the enhanced CO₂RR activity. EMIM-BF₄ plays other role(s). It is possible, in principle, for EMIM-BF₄, instead of H₂O, to serve as the h⁺ acceptor; however, if this were the case, then the CO₂RR activity would have been enhanced at higher EMIM-BF₄ concentrations, in line with a study of a different plasmon excitation-enhanced CO₂RR activity. EMIM*, the CO₂ moiety is structurally pre-configured for e⁻ acceptance. Consistent with this finding, 1e⁻ addition to [EMIM*-CO₂] is much more favorable as compared with 1e⁻ addition to CO₂ (Fig. 3c, d). Thus, it appears that EMIM-BF₄ can promote the transfer of photogenerated e⁻ from the Au NP to adsorbed CO₂, which is otherwise a major kinetic bottleneck in the photocatalytic reduction process. Furthermore, it is plausible that the CO₂⁻ anion radical formed on the Au surface by photoinitiated e⁻ transfer process has an enhanced lifetime due to solvation or complexation by EMIM⁺ (Fig. 3e). A longer lifetime of this reactive intermediate would increase the probability of C–C coupling between the intermediates.

**Empirical kinetic model.** Although the DFT computations provide insight into the central role of EMIM-BF₄ in CO₂ activation, the volcano-type dependence of the CO₂RR activity on the IL concentration deserves an explanation. From the hydrolysis of EMIM-BF₄ known from past studies47–50:

\[
\text{EMIM}^- + \text{CO}_2 \rightarrow [\text{EMIM}^-\text{CO}_2] + \text{H}^+
\]

(2)

we postulate a rate determining step in the reaction of CO₂
and H2O:

$$\text{EMIM}^- \text{BF}_4^- + \text{CO}_2 + x\text{H}_2\text{O} \rightarrow [\text{EMIM}^-\text{CO}_2]^- + \text{BF}_4^- - (x+1)\text{H}^+ + x\text{F}^-$$  \hspace{1cm} (3)

From this reaction equation, the concentration of the activated CO2 complex, [EMIM*-CO2], is expected to be directly proportional to [H+]x+1. Therefore, the [H+] determined from the measured pH of the EMIM-BF4 solution (Supplementary Fig. 23) serves as a proxy for the concentration of [EMIM*-CO2], based on which the [EMIM*-CO2] concentration is expected to be the highest in the EMIM-BF4 concentration range around 5 mol%. The higher the concentration of the activated [EMIM*-CO2] complex, the greater is the rate of CO2 conversion and also the higher the likelihood of C-C coupling required for C2 production. Therefore, both the overall activity and the selectivity in favor of C2 products are favorable in the 3–7 mol% EMIM-BF4 range, with the most optimal performance achieved at 5 mol% EMIM-BF4. On the other hand, the activated complex has zero concentration in pure water on one extreme and in pure EMIM-BF4 on the other extreme, which explains the nil turnover at these conditions. An additional reason for the drop in activity at higher EMIM-BF4 concentrations may be that the adsorption of BF4− to the Au NP surface (Supplementary Fig. 26) dominates at these concentrations to such an extent that the adsorption of CO2 and/or [EMIM*-CO2] to the Au surface is largely inhibited and so is the e− transfer to CO2.

The CO2RR activity depends on the concentration of this activated complex to a high reaction order. This is best exemplified by the plots of TOF for each hydrocarbon as a function of the [H+] (Fig. 4a–e), which as explained above, serves as a proxy for the concentration of [EMIM*-CO2]. The pseudo-reaction order, n, is found to be 1.9 for C2H4, 2.5 for C2H2, 4.0 for C3H6, and 4.0 for C3H8. The fit for the CH4 TOF has a relatively high χ2-value, so the n of 2.7 estimated for CH4 has a lower confidence. In general, the pseudo-reaction order is higher for the longer hydrocarbons, which perhaps captures the need for multiple activated complexes to be available for undergoing coupling to C2 and C3 fragments. The high pseudo-reaction order for the C3 products goes hand-in-hand with an apparent volcano trend with respect to the EMIM-BF4 concentration, mirroring closely the trend in the TOF for that hydrocarbon (Fig. 4f).

Thus, we reported the green-light-driven synthesis of C1–C3 hydrocarbons from CO2 and water on plasmonic Au NPs in an IL medium. The resonant green light absorption of the plasmonic NPs and their ability to sustain electrostatically charged surfaces under resonant CW excitation are at the heart of the observed photoreactivity. The IL plays a synergistic role due to its complexation with the CO2, which preconfigures the CO2 for accepting e− from photoexcited Au NPs. The enhanced reactivity of CO2 in the presence of the IL obviates the need for an applied potential or a sacrificial scavenger. Although hydrocarbon production yields in the reaction need further optimization, the generation of propane by overall 20e−+20H+ reduction and coupling of three CO2 molecules is both striking and mechanistically rich. The precise intermediates and reaction pathways, including C–C coupling and dehydrogenation steps, which yield each of the hydrocarbons, deserve further elucidation. Beyond CO2 conversion studied here, ILs may have promise in other photocatalytic schemes where activation of relatively inert
substrates and stabilization of high-energy charged intermediates is desirable.

Data availability

All raw images and source data are available from the authors upon reasonable request.

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References

1. Lewis, N. S. & Nocera, D. G. Powering the planet: chemical challenges in solar energy utilization. Proc. Natl Acad. Sci. USA 103, 15729–15735 (2006).
2. Olah, G. A., Prakash, G. K. S. & Goeppert, A. Anthropogenic chemical carbon cycle for a sustainable future. J. Am. Chem. Soc. 133, 12881–12898 (2011).
3. Chu, S. & Majumdar, A. Opportunities and challenges for a sustainable energy future. Nature 488, 294–302 (2012).
4. Lewis, N. S. Research opportunities to advance solar energy utilization. Science 351, 353 (2016).
5. Bai, S. et al. Highly active and selective hydrogenation of CO2 to ethanol by ordered Pd–Cu Nanoparticles. J. Am. Chem. Soc. 139, 6827–6830 (2017).
6. Xie, C. et al. Tandem catalysis for CO2 hydrogenation to C2–C4 hydrocarbons. Nano Lett. 17, 3798–3802 (2017).
7. Kattel, S., Ramirez, P. J., Chen, J. G., Rodriguez, J. A. & Liu, P. Active sites for CO2 hydrogenation to methanol on Cu2ZnO catalysts. Science 355, 1296–1299 (2017).
8. Vogt, C. et al. Unravelling structure sensitivity in CO2 hydrogenation over nickel. Nat. Catal. 1, 127–134 (2018).
9. Jiang, K. et al. Metal ion cycling of Cu foil for selective C–C coupling in electrochemical CO2 reduction. Nat. Catal. 1, 111–119 (2018).
10. He, J., Dettlaff-Bach, K. E., Salvatore, D. A., Li, T. & Berlinguette, C. P. High throughput synthesis of mixed-metal electrocatalysts for CO2 reduction. Angew. Chem. Int. Ed. 56, 6068–6072 (2017).
11. Kuhl, K. P. et al. Electro catalytic conversion of carbon dioxide to methane and methanol on transition metal surfaces. J. Am. Chem. Soc. 136, 14107–14113 (2014).
12. Resasco, J. et al. Promoter effects of alkali metal cations on the electrochemical reduction of carbon dioxide. J. Am. Chem. Soc. 139, 11277–11287 (2017).
13. Manthiram, K., Surendranath, Y. & Alivisatos, A. P. Dendritic assembly of gold nanoparticles during fuel-forming electrocatalysis. J. Am. Chem. Soc. 136, 7237–7240 (2014).
14. Wuttig, A., Yoon, Y., Ryu, J. & Surendranath, Y. Bicarbonate is not a general acid in Au-catalyzed CO2 electroreduction. J. Am. Chem. Soc. 139, 17199–17213 (2017).
15. Wuttig, A., Yaguchi, M., Motohayashi, K., Osawa, M. & Surendranath, Y. Inhibited proton transfer enhances Au-catalyzed CO2-to-fuels selectivity. Proc. Natl Acad. Sci. USA 113, E4585–E4593 (2016).
16. Liu, M. et al. Enhanced electrocatalytic CO2 reduction via field-induced reagent concentration. Nature 537, 382–386 (2016).
17. Mariano, R. G., McKelvey, K., White, H. S. & Kanan, M. W. Selective increase in CO2 electroreduction activity at grain-boundary surface terminations. Science 358, 1187–1192 (2017).
18. Zeng, G. et al. Enhanced photocatalytic reduction of CO2 to CO through TiO2 passivation of InP in liquidics. Chem. Eur. J. 21, 13502–13507 (2015).
19. Xing, M. et al. Modulation of the reduction potential of TiO2 by fluorination for efficient and selective CH4 generation from CO2 photoreduction. Nano Lett. 18, 4–10 (2018).
20. Park, H., Ou, H. H., Colussi, A. J. & Hoffmann, M. R. Artificial photosynthesis of C3–C4 hydrocarbons from water and CO2 on titane nanotubes decorated with nanoparticle elemental copper and CuS quantum dots. J. Phys. Chem. A 119, 4658–4666 (2015).
21. Rao, H., Schmidt, L. C., Bonin, J. & Robert, M. Visible-light-driven methane formation from CO2 with a molecular iron catalyst. Nature 548, 74–77 (2017).
22. Niu, K. et al. A sponge nickel-organic CO2 reduction photocatalyst for nearly 100% selective CO production. Sci. Adv. 3, e1700921 (2017).
23. Neatu, Ş., Maciá-Agulló, J. A., Concepción, P. & Garcia, H. Gold–copper nanoalloys supported on TiO2 as photocatalysts for CO2 reduction by water. J. Am. Chem. Soc. 136, 15969–15976 (2014).
24. Zhang, X. et al. Plasmon-enhanced catalysis: distinguishing thermal and nonthermal effects. Nano Lett. 18, 1714–1723 (2018).
25. Zhang, X. et al. Product selectivity in plasmonic photocatalysis for carbon dioxide hydrogenation. Nat. Commun. 8, 14542 (2017).
26. DuChene, J. S., Tagliabue, G., Welch, A. J., Cheng, W. H. & Atwater, H. A. Hot hole collection and photoelectrochemical CO2 reduction with plasmonic Au/p-GaN photocathodes. Nano Lett. 18, 2545–2550 (2018).
27. Hou, W., Pavaskar, P., Goeppert, A., Aykol, M. & Cronin, S. B. Photocatalytic conversion of CO2 to hydrocarbon fuels via plasmon-enhanced absorption and metallic interband transitions. ACS Catal. 1, 929–936 (2011).
28. Yu, S., Wilson, A. J., Hee, J. & Jain, P. K. Plasmonic control of multi-electron transfer and C–C coupling in visible-light-driven CO2 reduction on Au nanoparticles. Nano Lett. 18, 2189–2194 (2018).
29. Yu, S., Wilson, A. J., Kumari, G., Zhang, X. & Jain, P. K. Opportunities and challenges of solar-energy-driven carbon dioxide to fuel conversion with plasmonic catalysts. ACS Energy Lett. 2, 2058–2070 (2017).
30. Yang, J., Guo, Y., Lu, W., Jiang, R. & Wang, J. Emerging applications of plasmons in driving CO2 reduction and N2 fixation. Adv. Mater. 30, 1802227 (2018).
31. Calle-Vallejo, F. & Koper, M. T. M. Theoretical considerations on the electroreduction of CO2 to C2 species on Cu(100) electrodes. Angew. Chem. Int. Ed. 52, 7282–7285 (2013).
32. Nie, X., Esopi, M. R., Janik, M. J. & Asthagiri, A. Selectivity of CO₂ reduction on copper electrodes: the role of the kinetics of elementary steps. Angew. Chem. Int. Ed. 52, 2459–2462 (2013).

33. Chen, Y., Li, C. W. & Kanan, M. W. Aqueous CO₂ reduction at very low overpotential on oxide-derived Au nanoparticles. J. Am. Chem. Soc. 134, 19969–19972 (2012).

34. Kim, Y., Dunnett Torres, D. & Jain, P. K. Activation energies of plasmonic catalysts. Nano Lett. 16, 3399–3407 (2016).

35. Rosen, B. A. et al. The nature of plasmonically assisted hot-electron transfer in a donor-bridge-acceptor complex. ACS Catal. 7, 4360–4365 (2017).

36. Kim, Y., Smith, J. G. & Jain, P. K. Harvesting multiple electron-hole pairs generated through plasmonic excitation of Au nanoparticles. Nat. Chem. 10, 763–769 (2018).

37. Rosen, Ba et al. Ionic liquid–mediated selective conversion of CO₂ to CO at low overpotentials. Science 334, 643–644 (2011).

38. García Rey, N. & Dlott, D. D. Structural transition in an ionic liquid electrochemical system: a theoretical study. J. Phys. Chem. C 119, 20892–20899 (2015).

39. Sun, L., Ramesha, G. K., Kamat, P. V. & Brennecke, J. F. Switching the reaction course of electrochemical CO₂ reduction with ionic liquids. Langmuir 30, 6302–6308 (2014).

40. Asadi, M. et al. Nanostructured transition metal dichalcogenide electrocatalysts for CO₂ reduction in ionic liquid. Science 353, 467–470 (2016).

41. Rosen, B. A. et al. In situ spectroscopic examination of a low overpotential pathway for carbon dioxide conversion to carbon monoxide. J. Phys. Chem. C 116, 15307–15312 (2012).

42. Wang, Y. et al. Activation of CO₂ by ionic liquid EMIM–BF₄ in the electrochemical system: a theoretical study. Phys. Chem. Chem. Phys. 17, 23521–23531 (2015).

43. Fredlake, C. P., Crosthwaite, J. M., Hert, D. G., Aki, S. N. V. K. & Brennecke, J. F. Thermophysical properties of imidazolium-based ionic liquids. J. Chem. Eng. Data 49, 954–964 (2004).

44. Zhang, Y., Shi, C., Brennecke, J. F. & Maginn, E. J. Refined method for predicting electrochemical windows of ionic liquids and experimental validation studies. J. Phys. Chem. B 118, 6250–6255 (2014).

45. Zhou, M., Diwu, Z., Panchuk-Voloshina, N. & Hauaggl, R. P. A stable nonfluorescent derivative of resorufin for the fluorometric determination of trace hydrogen peroxide: applications in detecting the activity of phagocyte NADPH oxidase and other oxidases. Anal. Biochem. 253, 162–168 (1997).

46. Pera-Titus, M. Porous inorganic membranes for CO₂ capture: present and prospects. Chem. Rev. 114, 1413–1492 (2014).

47. Rosen, B. A., Zhu, W., Kaul, G., Salehi-Khojin, A. & Masel, R. J. Water enhancement of CO₂ conversion on silver in 1-ethyl-3-methylimidazolium tetrafluoroborate. J. Electrochem. Soc. 160, H138–H141 (2012).

48. Freire, M. G., Neves, C. M. S., Marruco, I. M., Coutinho, J. A. P. & Fernandes, A. M. Hydrolysis of tetrafluoroborate and hexafluorophosphate counter ions in imidazolium-based ionic liquids. J. Phys. Chem. A 114, 3744–3749 (2010).

49. Kumar, B. et al. Renewable and metal-free carbon nanofibre catalysts for carbon dioxide reduction. Nat. Commun. 4, 1–8 (2013).

50. Deerelefs, M., Pittner, W. R. & Hardacre, C. Quantification of halide in ionic liquids using ion chromatography. Anal. Chem. 76, 2118–2123 (2004).

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Author contributions

S.Y. performed all experimental studies, DFT computations, and data-analysis, and co-wrote the manuscript. P.K.J. conceived project and designed studies, analyzed results, and co-wrote the manuscript.

Additional information

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