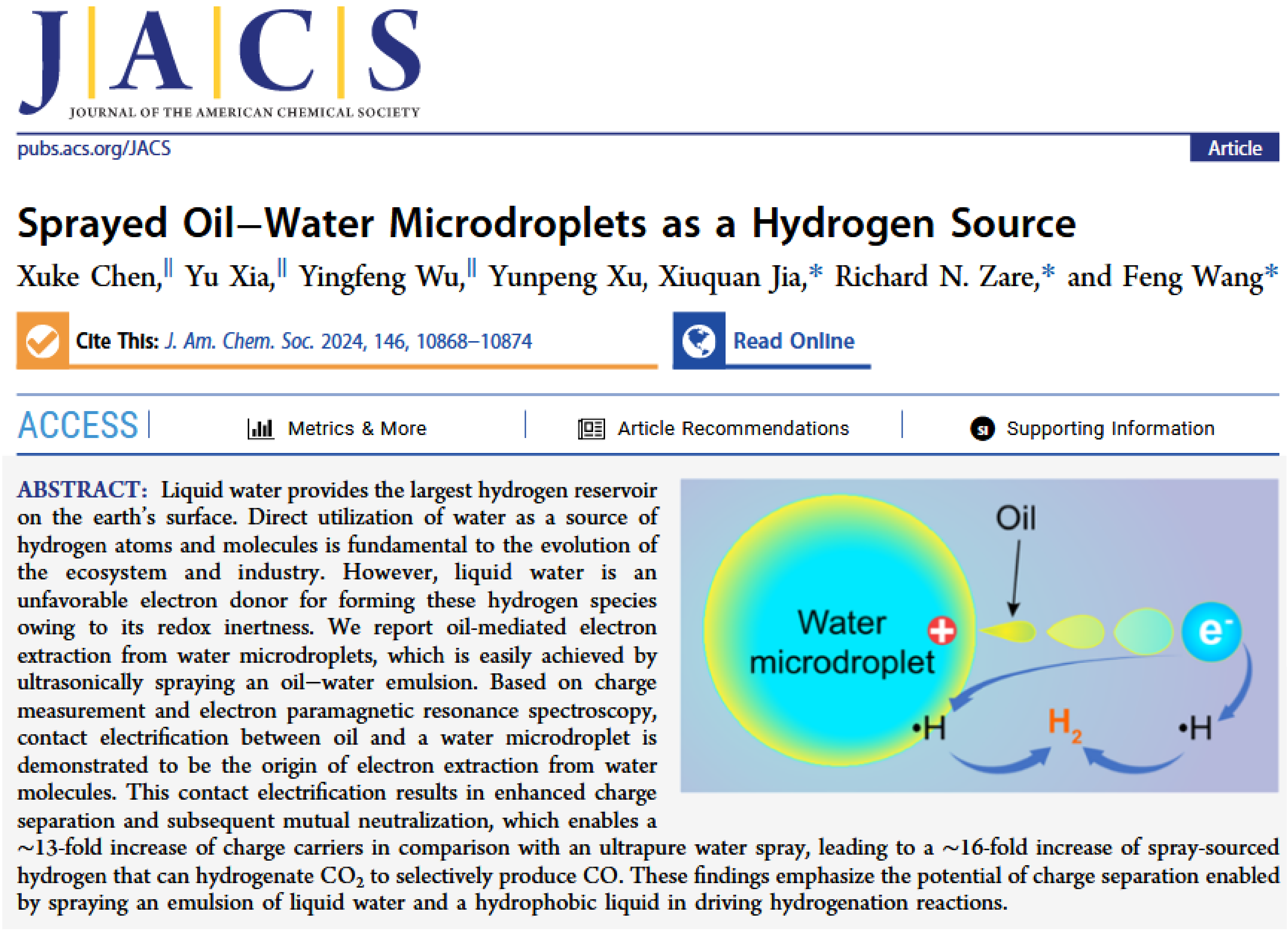
# PAPER PRESENTATION



JOURNAL OF THE AMERICAN CHEMICAL SOCIETY
pubs.acs.org/JACS
Article

## Sprayed Oil–Water Microdroplets as a Hydrogen Source

Xuke Chen,[‖] Yu Xia,[‖] Yingfeng Wu,[‖] Yunpeng Xu, Xiuquan Jia,* Richard N. Zare,* and Feng Wang*

**Cite This:** *J. Am. Chem. Soc.* 2024, 146, 10868–10874

Read Online

ACCESS | Metrics & More | Article Recommendations | Supporting Information

**ABSTRACT:** Liquid water provides the largest hydrogen reservoir on the earth's surface. Direct utilization of water as a source of hydrogen atoms and molecules is fundamental to the evolution of the ecosystem and industry. However, liquid water is an unfavorable electron donor for forming these hydrogen species owing to its redox inertness. We report oil-mediated electron extraction from water microdroplets, which is easily achieved by ultrasonically spraying an oil–water emulsion. Based on charge measurement and electron paramagnetic resonance spectroscopy, contact electrification between oil and a water microdroplet is demonstrated to be the origin of electron extraction from water molecules. This contact electrification results in enhanced charge separation and subsequent mutual neutralization, which enables a ~13-fold increase of charge carriers in comparison with an ultrapure water spray, leading to a ~16-fold increase of spray-sourced hydrogen that can hydrogenate $CO_2$ to selectively produce CO. These findings emphasize the potential of charge separation enabled by spraying an emulsion of liquid water and a hydrophobic liquid in driving hydrogenation reactions.

## Published on:
## 4th April, 2024

**Corresponding Authors**

**Xiuquan Jia** – *State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, P. R. China;* orcid.org/0000-0002-9921-234X; Email: jiaxiuquan@dicp.ac.cn

**Richard N. Zare** – *Department of Chemistry, Stanford University, Stanford, California 94305, United States;* orcid.org/0000-0001-5266-4253; Email: zare@stanford.edu

**Feng Wang** – *State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, P. R. China; University of Chinese Academy of Sciences, Beijing 100049, P. R. China;* orcid.org/0000-0002-9167-8743; Email: wangfeng@dicp.ac.cn

## By:
## ANUBHAV MAHAPATRA

# Outline

- Introduction
- Why this paper?
- Background
- Results and Discussion
- Conclusions
- Future Directions

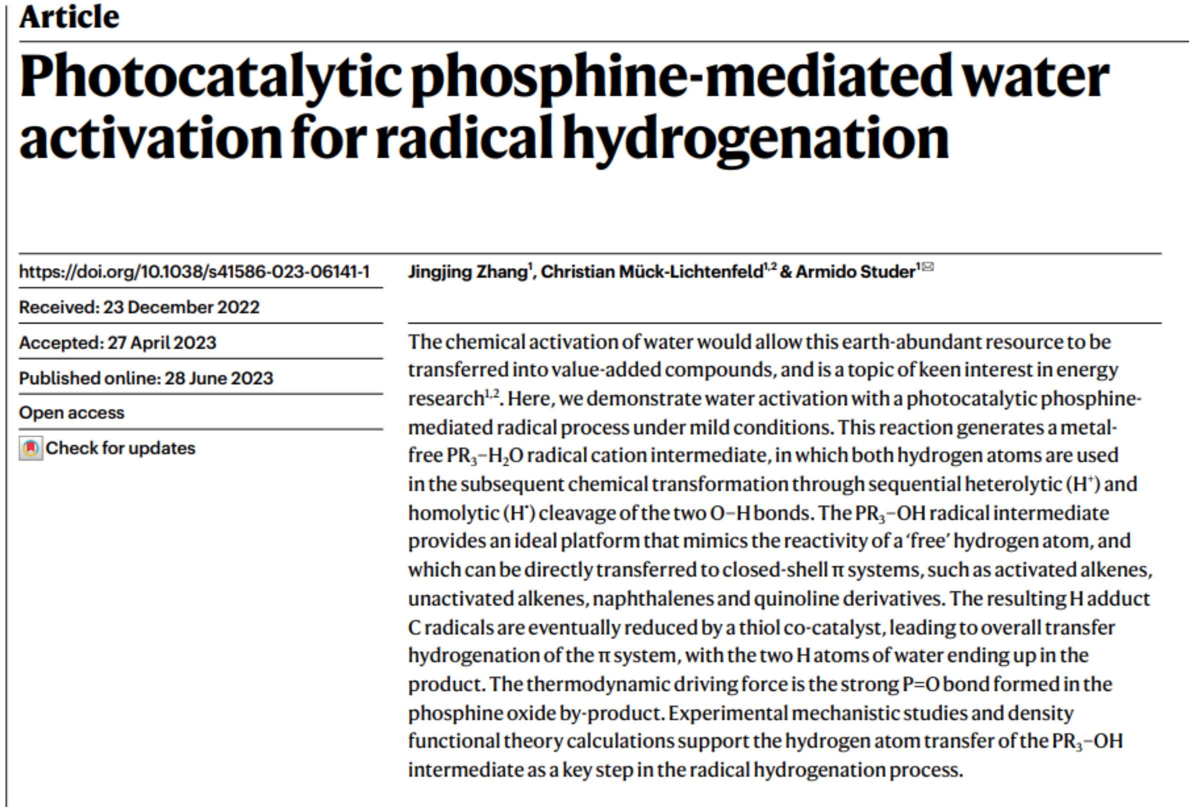
# Introduction

- Liquid water is Earth's **largest surface reservoir of hydrogen**. Using water directly as a source of hydrogen atoms and molecules is essential for ecosystem development and industrial progress.
- **Oil-water mixtures from spills** cause significant environmental harm and $CO_2$ emissions, highlighting the urgent need for eco-friendly solutions to degrade or repurpose these mixtures toward net-zero carbon goals.
- Water is **highly resistant to redox reactions** due to the high thermodynamic potential (1.23 V) needed to split it into $H_2$ and $O_2$, making it challenging to utilize as a source of hydrogen.
- In contrast to bulk water, microdroplets have been shown in numerous studies to **generate a strong electric field at their interface**, sufficient to spontaneously ionize $OH^-$ ions and release free electrons.
- Conversion processes include the fixation of $N_2$ into ammonia and urea, $CO_2$ fixation via the reverse tricarboxylic acid cycle, and the production of formic acid from $CO_2$ require selective hydrogenation.
- This study found that **ultrasonic spraying** an oil-water mixture induces contact electrification, enabling electron extraction from microdroplets and producing approximately **13 times** more charge carriers than ultrapure water spray.
- The **increased charge separation** boosts **hydrogen evolution** from water spray by about **16-fold,** a capacity that selectively hydrogenates $CO_2$ to produce CO and other products.

# Why this paper?

- ✓ This study examines both the **spray and cavitation processes**, revealing how oil mediates electron extraction from water microdroplets in sprayed system **markedly increase the hydrogenation reaction** and not vice-versa.
- ✓ The study discusses sustainable method for converting $CO_2$ to selectively produce CO, aiming to reduce atmospheric carbon dioxide levels.

# Background



**Article**

## Photocatalytic phosphine-mediated water activation for radical hydrogenation

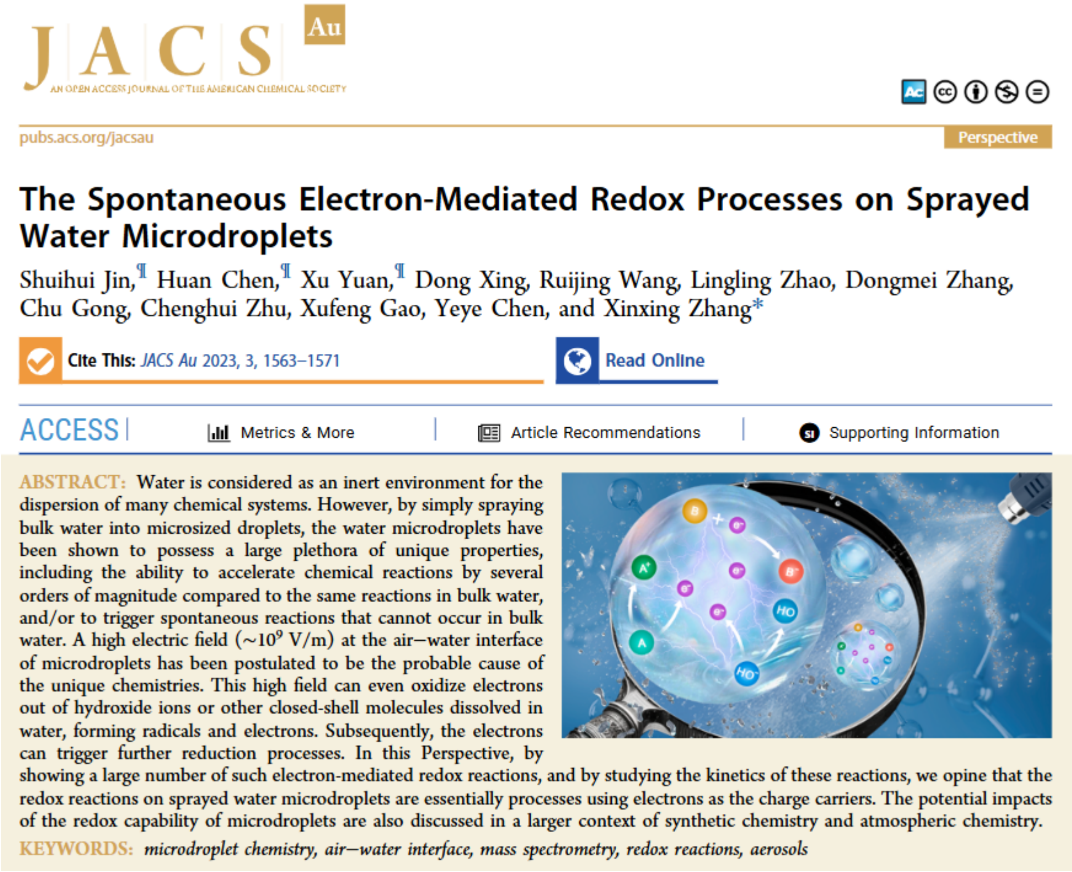
https://doi.org/10.1038/s41586-023-06141-1

Received: 23 December 2022

Accepted: 27 April 2023

Jingjing Zhang[1], Christian Mück-Lichtenfeld[1,2] & Armido Studer[1] ✉

The chemical activation of water would allow this earth-abundant resource to be transferred into value-added compounds, and is a topic of keen interest in energy research[1,2]. Here, we demonstrate water activation with a photocatalytic phosphine-mediated radical process under mild conditions. This reaction generates a metal-free $PR_3$–$H_2O$ radical cation intermediate, in which both hydrogen atoms are used in the subsequent chemical transformation through sequential heterolytic ($H^+$) and homolytic ($H^\bullet$) cleavage of the two O–H bonds. The $PR_3$–OH radical intermediate provides an ideal platform that mimics the reactivity of a 'free' hydrogen atom, and which can be directly transferred to closed-shell π systems, such as activated alkenes, unactivated alkenes, naphthalenes and quinoline derivatives. The resulting H adduct C radicals are eventually reduced by a thiol co-catalyst, leading to overall transfer hydrogenation of the π system, with the two H atoms of water ending up in the product. The thermodynamic driving force is the strong P=O bond formed in the phosphine oxide by-product. Experimental mechanistic studies and density functional theory calculations support the hydrogen atom transfer of the $PR_3$–OH intermediate as a key step in the radical hydrogenation process.



JACS Au
AN OPEN ACCESS JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

pubs.acs.org/jacsau

Perspective

## The Spontaneous Electron-Mediated Redox Processes on Sprayed Water Microdroplets

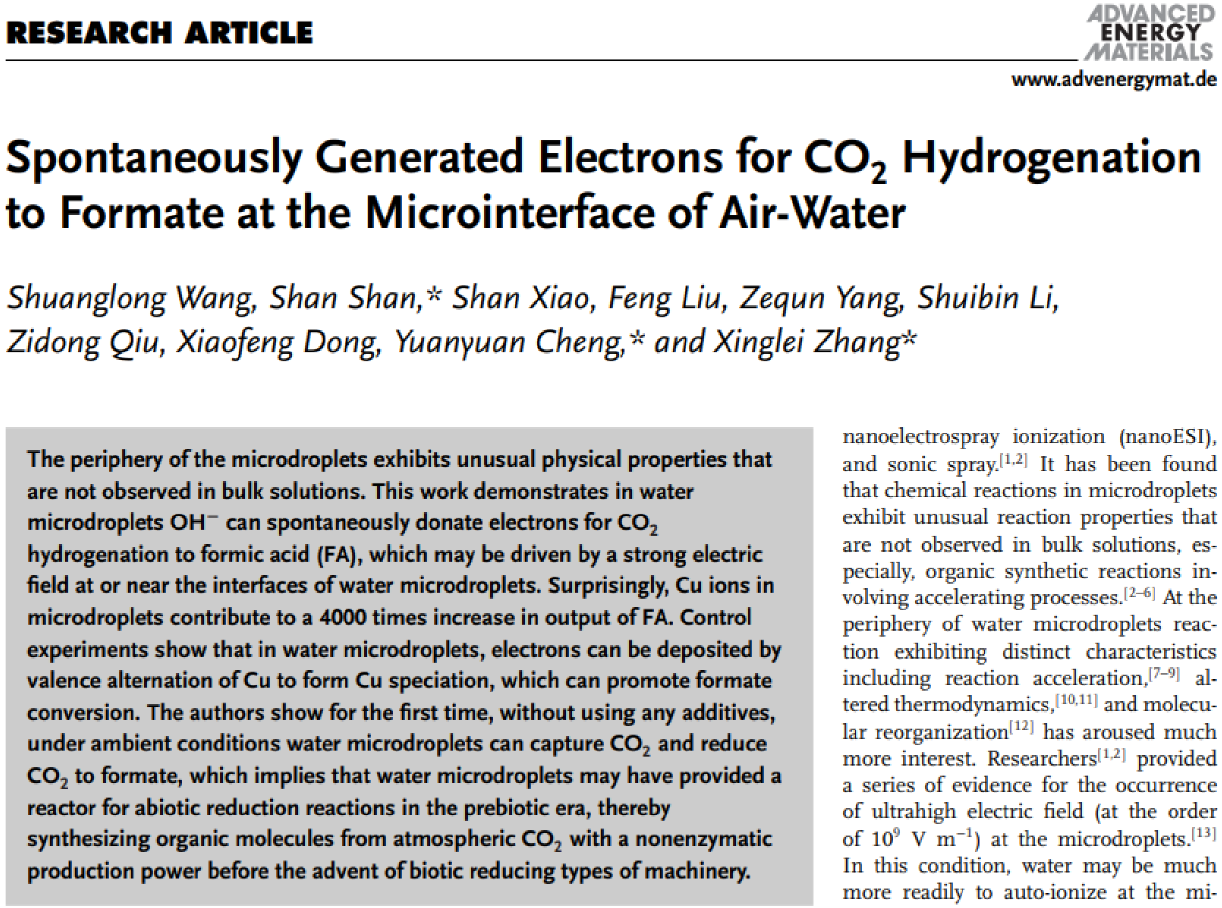
Shuihui Jin,[¶] Huan Chen,[¶] Xu Yuan,[¶] Dong Xing, Ruijing Wang, Lingling Zhao, Dongmei Zhang, Chu Gong, Chenghui Zhu, Xufeng Gao, Yeye Chen, and Xinxing Zhang*

Cite This: *JACS Au* 2023, 3, 1563–1571

ABSTRACT: Water is considered as an inert environment for the dispersion of many chemical systems. However, by simply spraying bulk water into microsized droplets, the water microdroplets have been shown to possess a large plethora of unique properties, including the ability to accelerate chemical reactions by several orders of magnitude compared to the same reactions in bulk water, and/or to trigger spontaneous reactions that cannot occur in bulk water. A high electric field (~$10^9$ V/m) at the air–water interface of microdroplets has been postulated to be the probable cause of the unique chemistries. This high field can even oxidize electrons out of hydroxide ions or other closed-shell molecules dissolved in water, forming radicals and electrons. Subsequently, the electrons can trigger further reduction processes. In this Perspective, by showing a large number of such electron-mediated redox reactions, and by studying the kinetics of these reactions, we opine that the redox reactions on sprayed water microdroplets are essentially processes using electrons as the charge carriers. The potential impacts of the redox capability of microdroplets are also discussed in a larger context of synthetic chemistry and atmospheric chemistry.

KEYWORDS: *microdroplet chemistry, air–water interface, mass spectrometry, redox reactions, aerosols*

# Background



**RESEARCH ARTICLE**

ADVANCED ENERGY MATERIALS

www.advenergymat.de

## Spontaneously Generated Electrons for $CO_2$ Hydrogenation to Formate at the Microinterface of Air-Water

*Shuanglong Wang, Shan Shan,* Shan Xiao, Feng Liu, Zequn Yang, Shuibin Li, Zidong Qiu, Xiaofeng Dong, Yuanyuan Cheng,* and Xinglei Zhang**

**The periphery of the microdroplets exhibits unusual physical properties that are not observed in bulk solutions. This work demonstrates in water microdroplets $OH^-$ can spontaneously donate electrons for $CO_2$ hydrogenation to formic acid (FA), which may be driven by a strong electric field at or near the interfaces of water microdroplets. Surprisingly, Cu ions in microdroplets contribute to a 4000 times increase in output of FA. Control experiments show that in water microdroplets, electrons can be deposited by valence alternation of Cu to form Cu speciation, which can promote formate conversion. The authors show for the first time, without using any additives, under ambient conditions water microdroplets can capture $CO_2$ and reduce $CO_2$ to formate, which implies that water microdroplets may have provided a reactor for abiotic reduction reactions in the prebiotic era, thereby synthesizing organic molecules from atmospheric $CO_2$ with a nonenzymatic production power before the advent of biotic reducing types of machinery.**

nanoelectrospray ionization (nanoESI), and sonic spray.[1,2] It has been found that chemical reactions in microdroplets exhibit unusual reaction properties that are not observed in bulk solutions, especially, organic synthetic reactions involving accelerating processes.[2–6] At the periphery of water microdroplets reaction exhibiting distinct characteristics including reaction acceleration,[7–9] altered thermodynamics,[10,11] and molecular reorganization[12] has aroused much more interest. Researchers[1,2] provided a series of evidence for the occurrence of ultrahigh electric field (at the order of $10^9$ V $m^{-1}$) at the microdroplets.[13] In this condition, water may be much more readily to auto-ionize at the mi-

Journal of Hazardous Materials 437 (2022) 129340

Contents lists available at ScienceDirect

Journal of Hazardous Materials

journal homepage: www.elsevier.com/locate/jhazmat

ELSEVIER

## Development of advanced oil/water separation technologies to enhance the effectiveness of mechanical oil recovery operations at sea: Potential and challenges

Bo Liu[a], Bing Chen[a,*], Jingjing Ling[a], Ethan James Matchinski[a], Guihua Dong[a], Xudong Ye[a], Fei Wu[a], Wanhua Shen[b], Lei Liu[c], Kenneth Lee[d], Lisa Isaacman[d], Stephen Potter[e], Brianna Hynes[a], Baiyu Zhang[a]

[a] *Northern Region Persistent Organic Pollution Control (NRPOP) Laboratory, Memorial University of Newfoundland, St. John's, NL A1B 3X5, Canada*
[b] *Environmental Engineering Program, University of Northern British Columbia, Prince George, BC V2N 4Z9, Canada*
[c] *Department of Civil and Resource Engineering, Dalhousie University, Halifax, NS B3H 4R2, Canada*
[d] *Ecosystem Science, Fisheries and Oceans Canada, Ottawa, ON K1A 0E6, Canada*
[e] *SL Ross Environmental Research Ltd., Ottawa, ON K2H 8S9, Canada*

# Results and Discussion

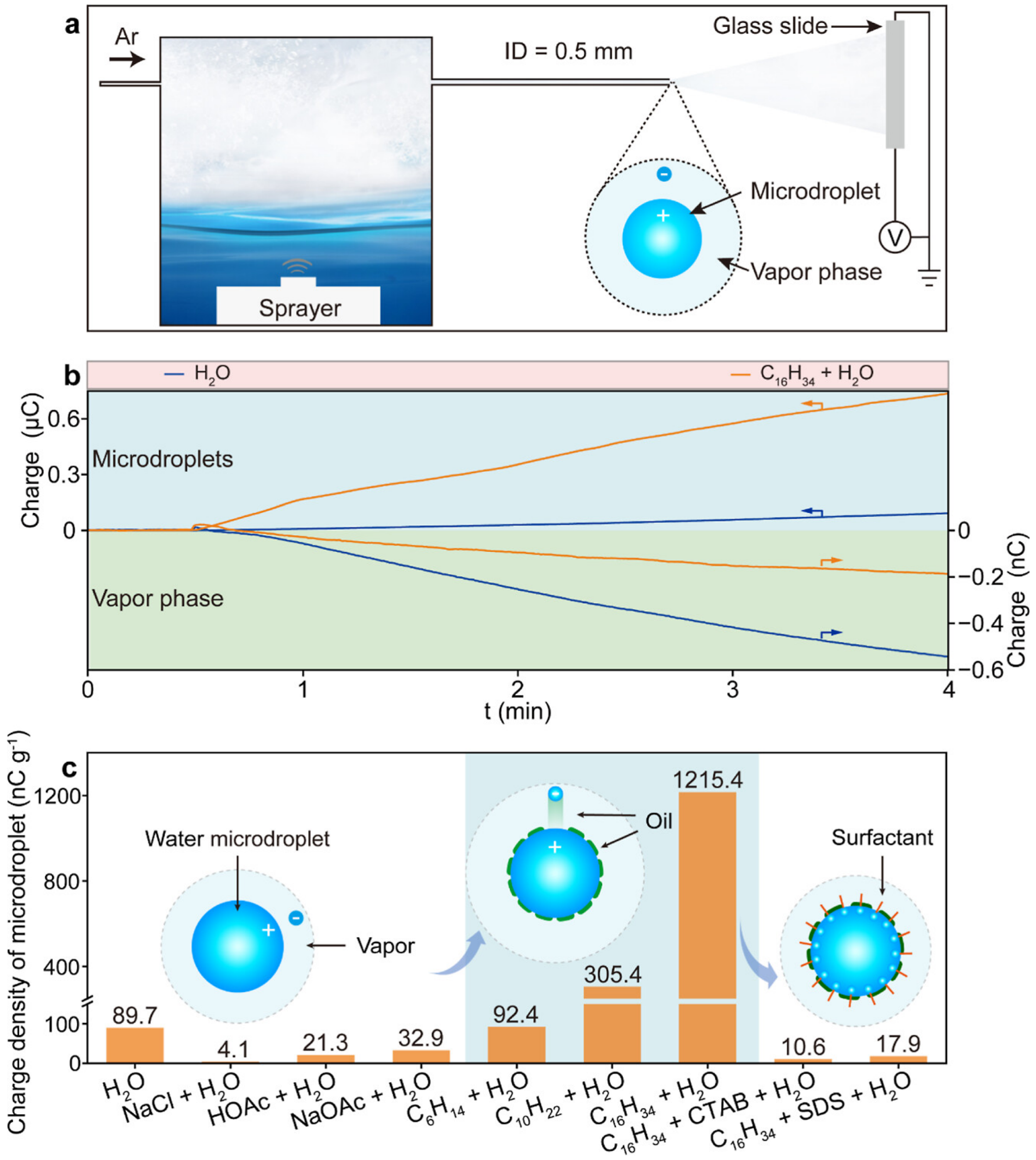


**Fig. 1** Sprayed hexadecane–water microdroplets and vapor phase.
(a) **Experimental setup.**
(b) **Charge measurements of microdroplets and the vapor phase.**
(c) **Measured electric charge density of microdroplets with additives.**

# Results and Discussion

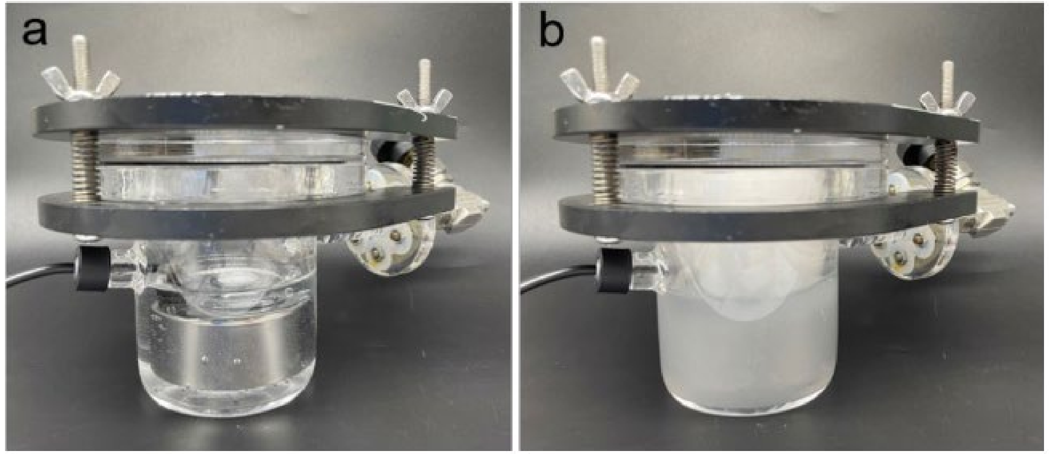


**Fig. S$_1$** Photographs of the experimental set-up **a)** before and **b)** during producing microdroplets.

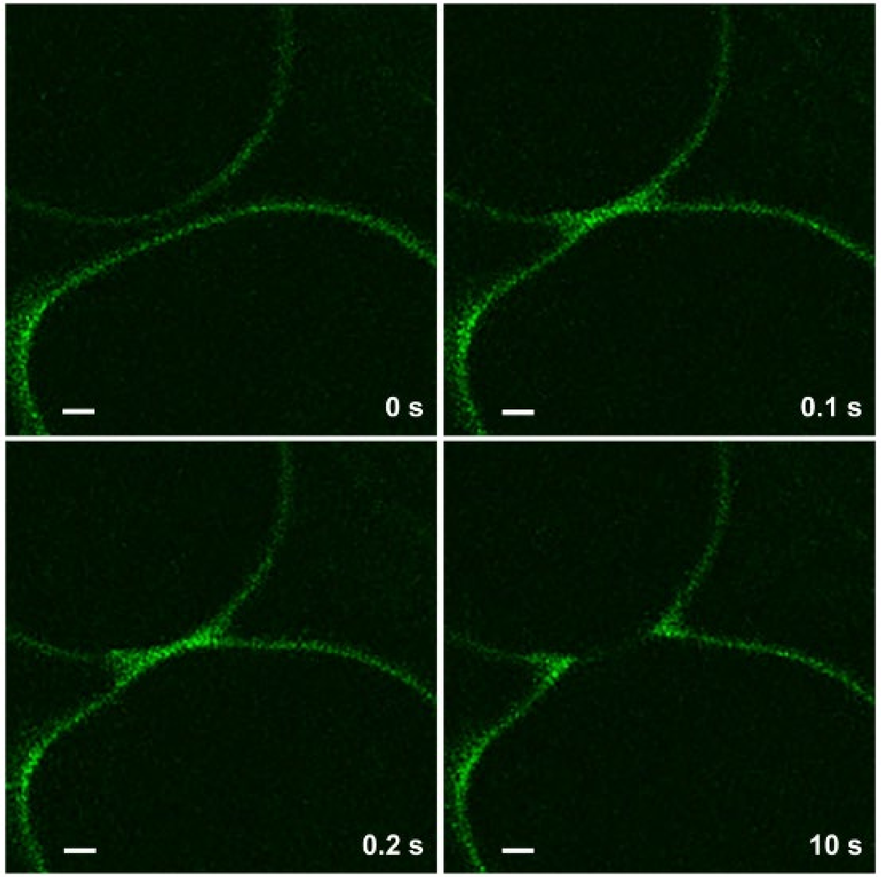


**Fig. S$_2$** Fluorescence images of hexadecane-SDS-water droplets showing the stable accumulation of oil on the surface of water droplets. Scale bars, **10 µm.**

# Results and Discussion

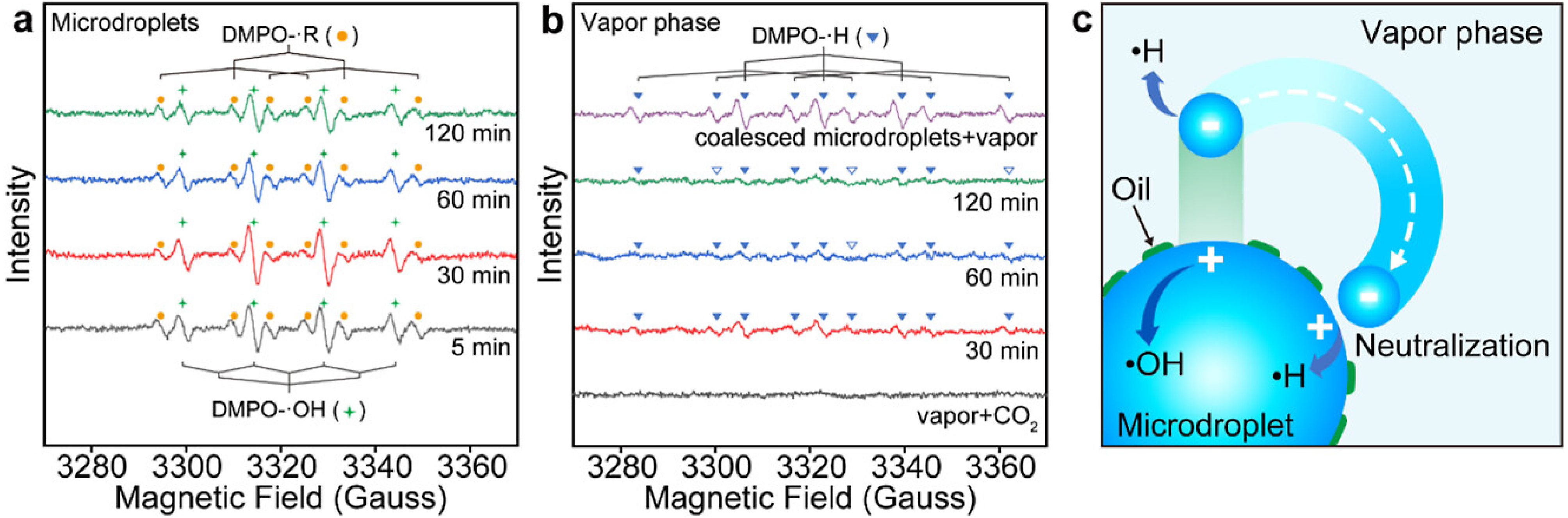


**Fig. 2** Observation of **radicals** formed in an **ultrasonic spray** (2.4 MHz and 24 W Ultrasonic frequency and power respectively) as detected by EPR spectroscopy in **(a)** microdroplets and the **(b)** vapor phase. **(c)** Schematic diagram of the mechanism for radical formation.

# Results and Discussion

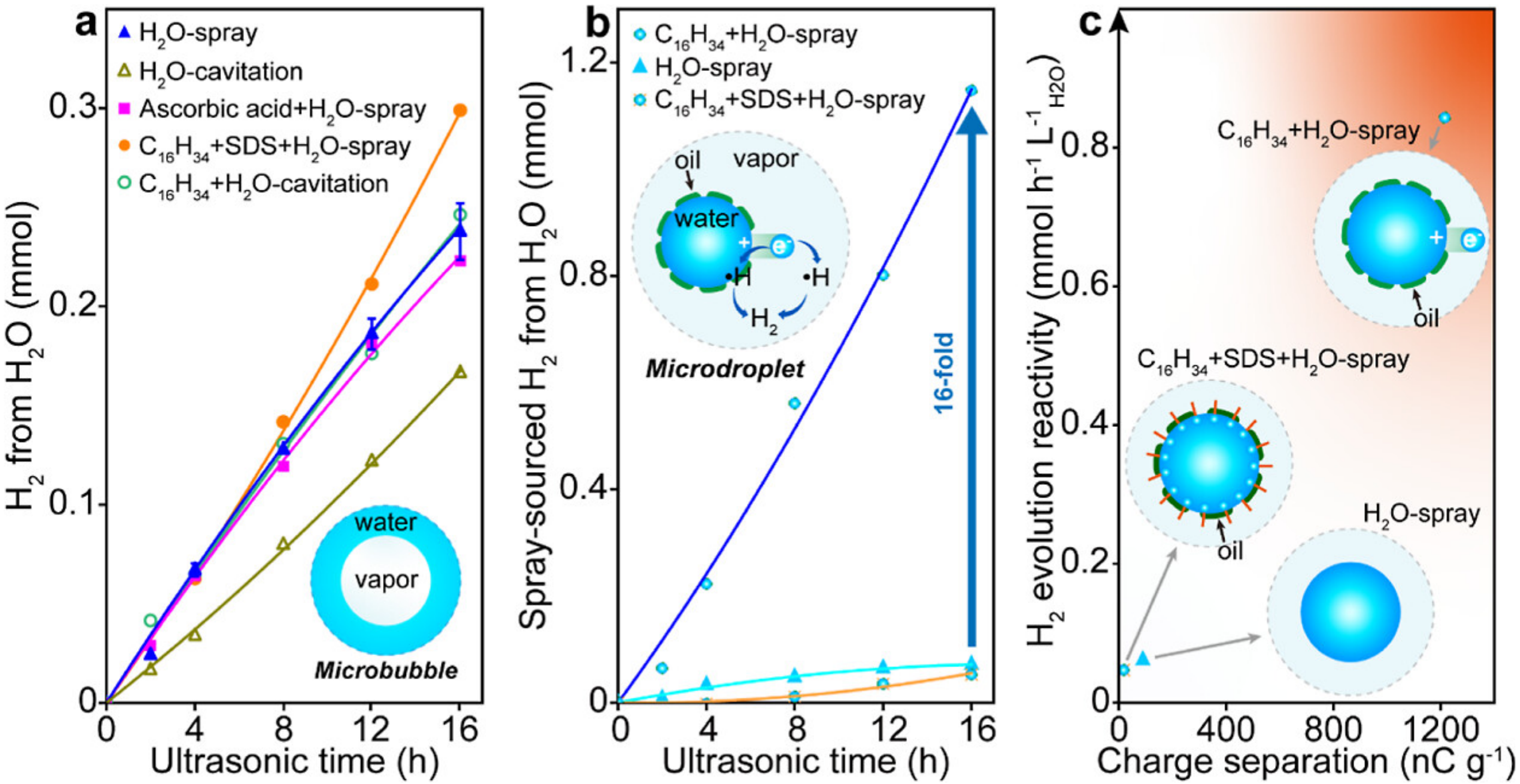


**Fig. 3** Evolution of **$H_2$.**

**(a)** Time courses of the $H_2$ product generated by **water spray and by water cavitation.**

**(b)** Comparison of a **spray-sourced $H_2$ product** generated from water in spraying a **hexadecane–water solution**, a **hexadecane–SDS–water solution, and ultrapure water**.

**(c)** Relationship **between charge separation of microdroplets** and spray-sourced $H_2$ evolution reactivity.

# Results and Discussion

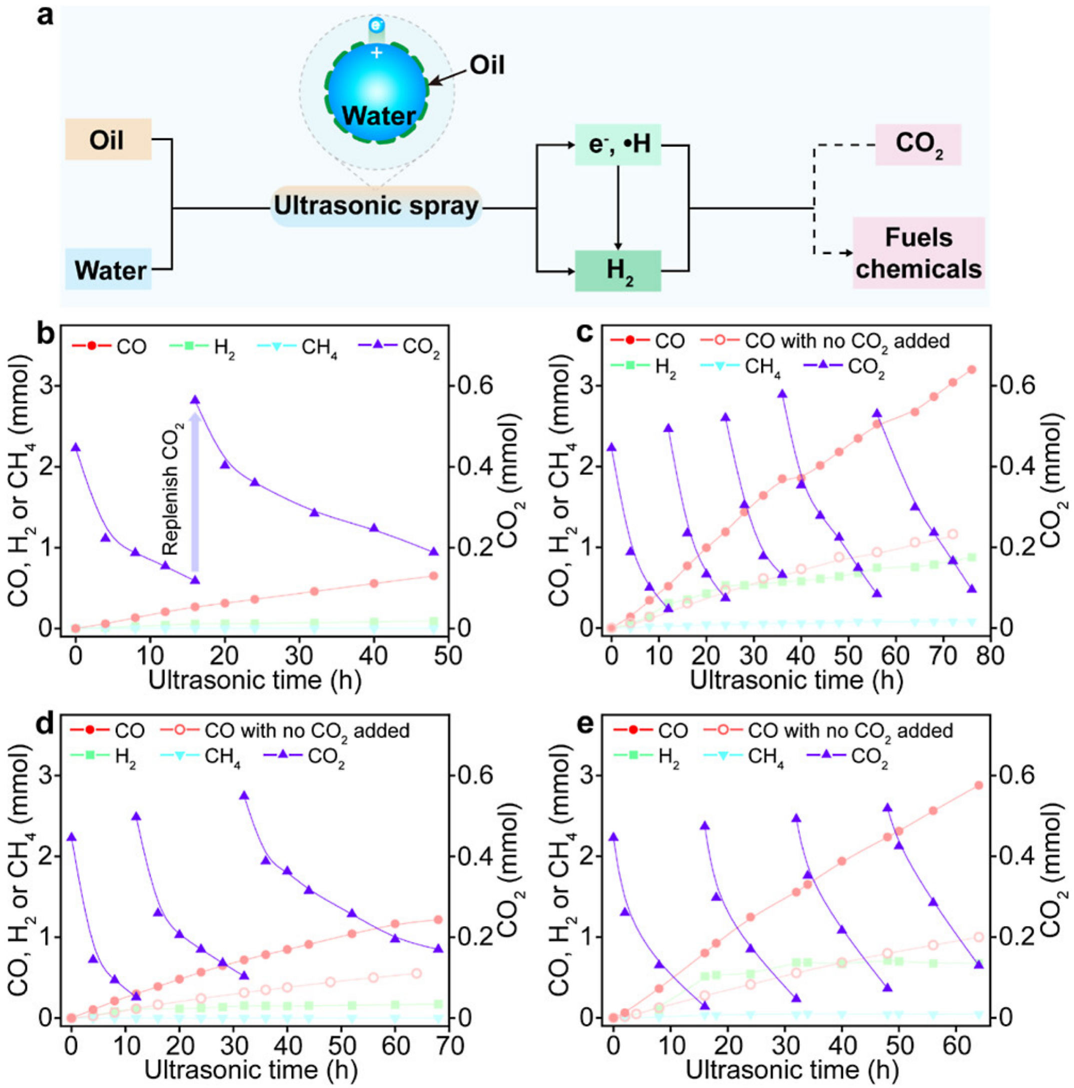


**Fig. 4 $CO_2$ hydrogenation reaction in oil–water systems**.

(a) Schematic overview of in situ utilization of electrons and reactive hydrogen species for $CO_2$ hydrogenation.

Time courses of **$CO_2$ hydrogenation** in an

**(b) Ultrapure water system** (70 mL $H_2O$),

**(c) hexadecane-water system** (70 mL $H_2O$ and 0.05 mL hexadecane),

**(d) soybean oil–water system** (70 mL $H_2O$ and **0.05 mL** soybean oil), and

**(e) soybean oil–water system** (70 mL $H_2O$ and **0.5 mL** soybean oil).

# Results and Discussion

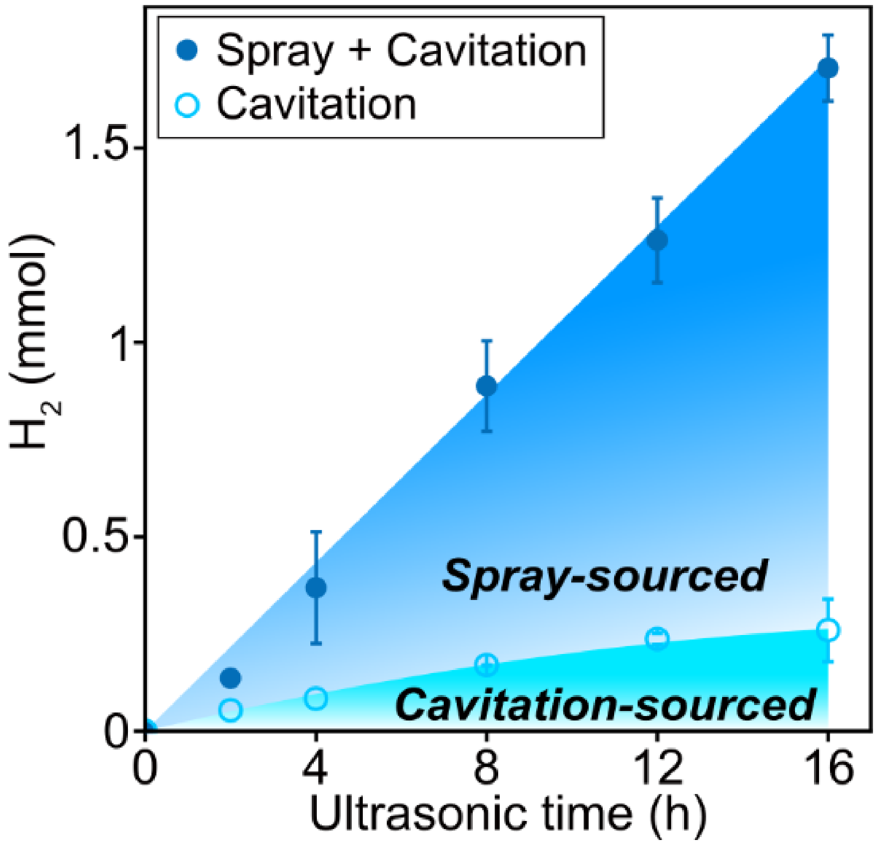


**Fig. $S_3$** Time courses of **$H_2$ product** generated from hexadecane-water system. Reaction conditions: 85 mL $H_2O$, 0.5 mL hexadecane, 2.4 MHz of ultrasonic frequency and 24 W of ultrasonic power, room temperature, 1 atm Ar.

# Results and Discussion

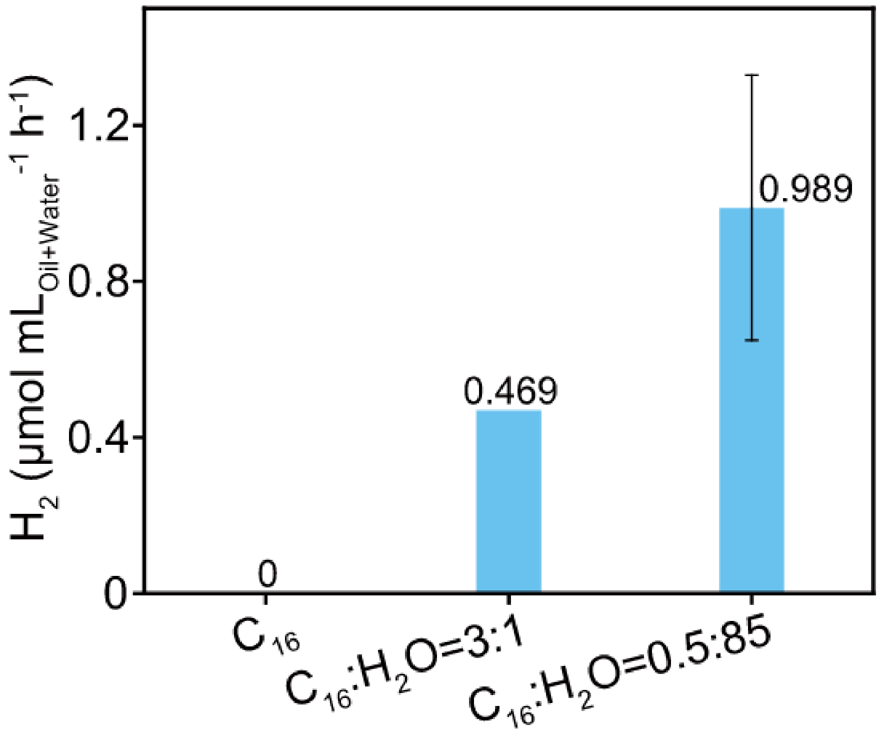


**Fig. $S_4$ Hydrogen formation** at varying oil-to-water ratios. **Reaction conditions**: **a)** 8 mL hexadecane in a sealed glass bottle, **b)** 6 mL hexadecane and 2 mL water in a sealed glass bottle, **c)** 0.5 mL hexadecane and 85 mL water in a sealed quartz reactor. 2.4 MHz of ultrasonic frequency and 24 W of ultrasonic power. The 20 mL glass bottle was placed at 1 cm above the ceramic disc of the ultrasonic transducer, which was immersed in a water bath.

# Results and Discussion

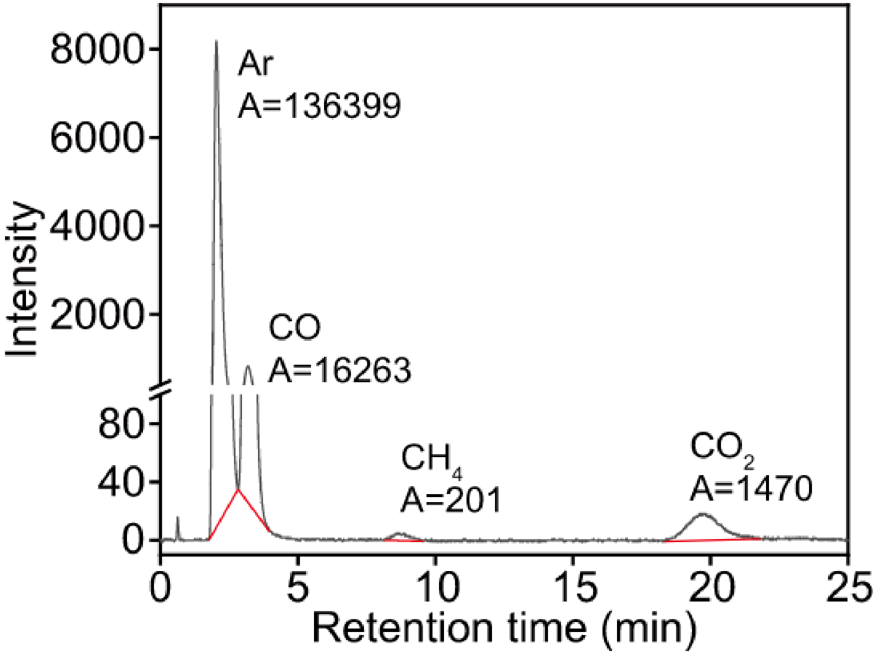


**Fig. $S_5$** GC spectrum of **C1 products** from sprayed hexadecane-water system. **Reaction conditions**: 70 mL $H_2O$, 0.05 mL hexadecane, a total of 50 mL $CO_2$ was added, 2.4 MHz of ultrasonic frequency and 24 W of ultrasonic power, room temperature, 1 atm Ar, 76 h.

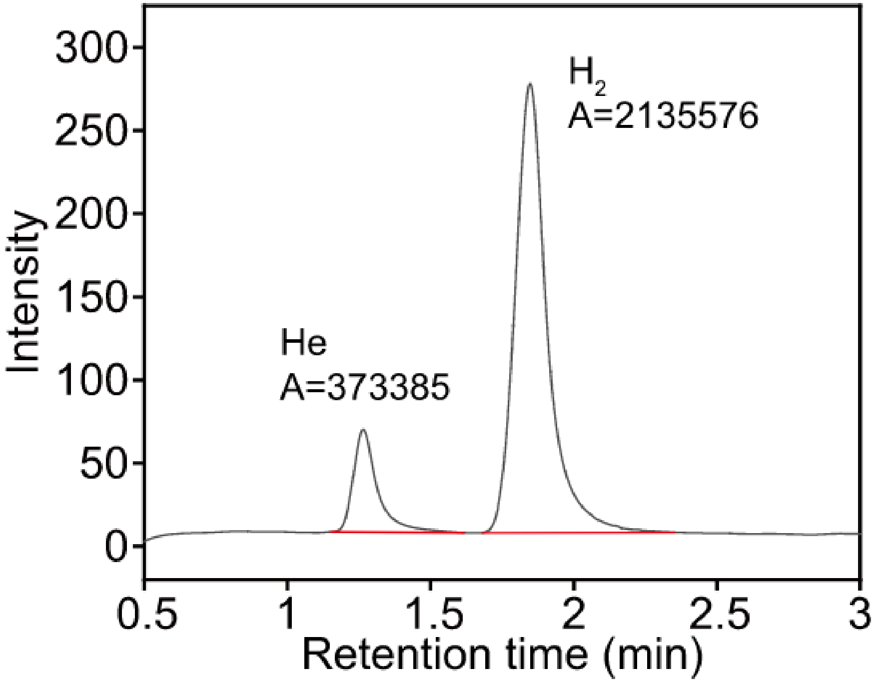


**Fig. $S_6$** GC spectrum of **$H_2$ product** from sprayed hexadecane-water system. **Reaction conditions**: 70 mL $H_2O$, 0.05 mL hexadecane, 2 mL He, a total of 50 mL $CO_2$ was added, 2.4 MHz of ultrasonic frequency and 24 W of ultrasonic power, room temperature, 1 atm Ar, 76 h.

# Conclusions

- ✓ In summary, these results reveal a mechanism that explains spray hydrogenation reactions that require charge separation.
- ✓ The charge separation of aqueous microdroplets was significantly enhanced due to the **oil-mediated extraction of electrons from sprayed microdroplets**.
- ✓ The reductive hydrogen species could further lead to an in situ $CO_2$ hydrogenation process run at normal temperature for selective CO formation using water as the hydrogen source.
- ✓ It extends the understanding of the interface of air-water in driving and accelerating chemistry.

# -THANK YOU