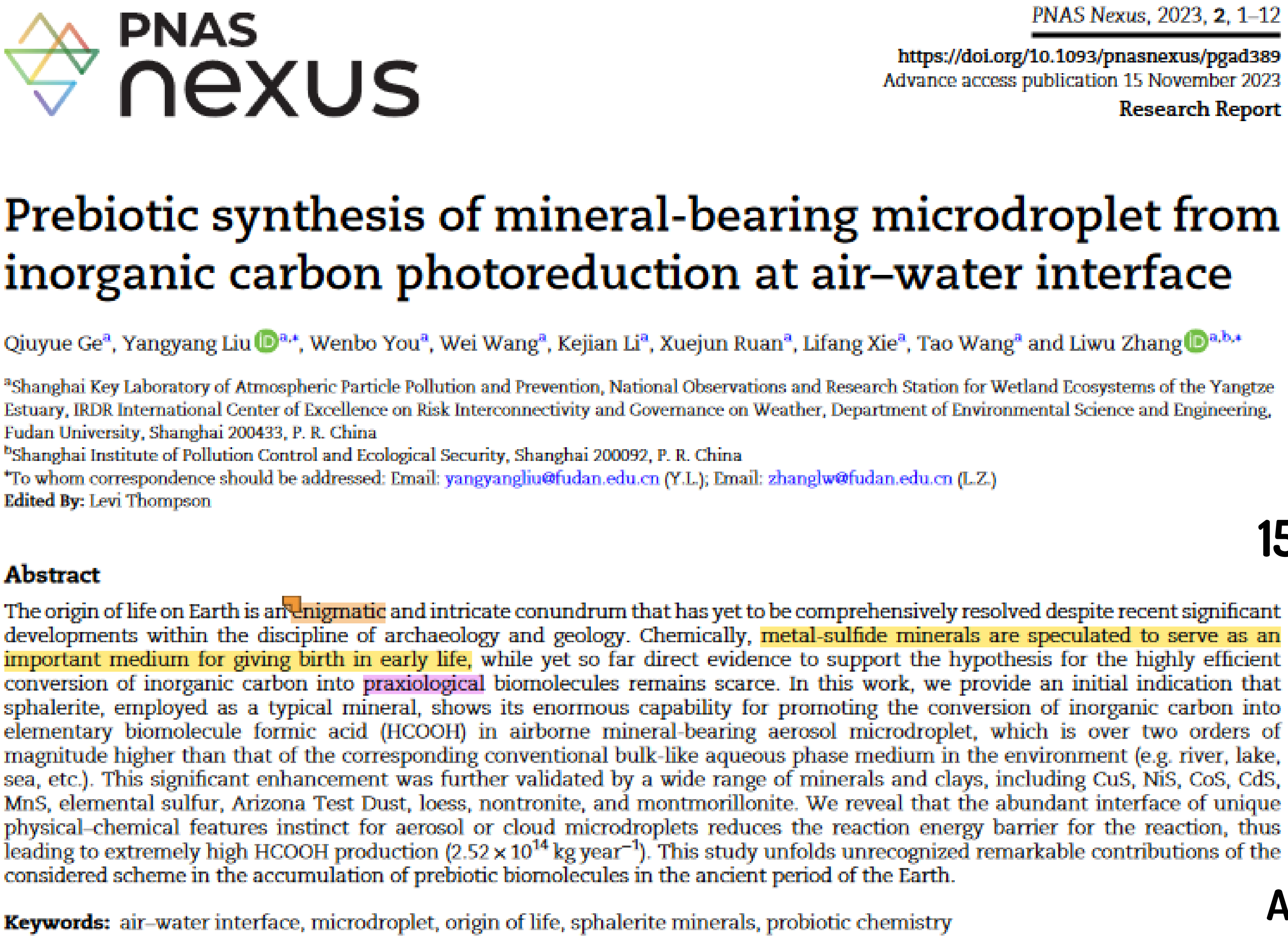
PAPER PRESENTATION



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Research Report

Prebiotic synthesis of mineral-bearing microdroplet from inorganic carbon photoreduction at air–water interface

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Edited By: Levi Thompson

Abstract

The origin of life on Earth is an enigmatic and intricate conundrum that has yet to be comprehensively resolved despite recent significant developments within the discipline of archaeology and geology. Chemically, metal-sulfide minerals are speculated to serve as an important medium for giving birth in early life, while yet so far direct evidence to support the hypothesis for the highly efficient conversion of inorganic carbon into praxiological biomolecules remains scarce. In this work, we provide an initial indication that sphalerite, employed as a typical mineral, shows its enormous capability for promoting the conversion of inorganic carbon into elementary biomolecule formic acid (HCOOH) in airborne mineral-bearing aerosol microdroplet, which is over two orders of magnitude higher than that of the corresponding conventional bulk-like aqueous phase medium in the environment (e.g. river, lake, sea, etc.). This significant enhancement was further validated by a wide range of minerals and clays, including CuS, NiS, CoS, CdS, MnS, elemental sulfur, Arizona Test Dust, loess, nontronite, and montmorillonite. We reveal that the abundant interface of unique physical–chemical features instinct for aerosol or cloud microdroplets reduces the reaction energy barrier for the reaction, thus leading to extremely high HCOOH production (2.52×10^{14} kg year^{-1}). This study unfolds unrecognized remarkable contributions of the considered scheme in the accumulation of prebiotic biomolecules in the ancient period of the Earth.

Keywords: air–water interface, microdroplet, origin of life, sphalerite minerals, probiotic chemistry

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Outline

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

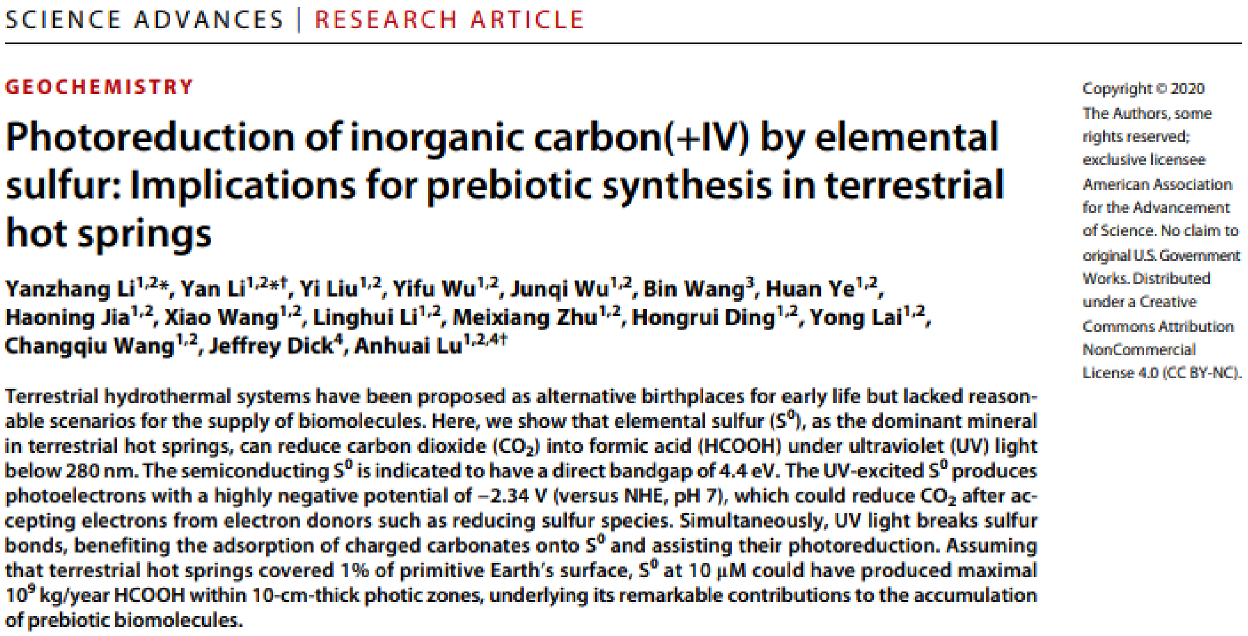
Introduction

- ✓ The **origin of life** on earth remains an elusive and complex issue that has yet to be fully revealed.
- ✓ The **conversion of inorganic carbon into basic organic molecules** is a pivotal step because it behaves as fundamental building blocks for any life forms.
- ✓ Formic acid (HCOOH) formed through **conventional slow heterogenous catalytic process** fails to explain the life origin by the time-consuming evolution. Therefore, a fast formation pathway needs to exist which can explain the unresolved life-origin mystery disputed for decade.
- ✓ The **abundant air-water interface from atmospheric aerosol microdroplets have already been proposed as prebiotic chemical reactors.**
- ✓ The environment of primitive earth was found to contain **lot of CO_2 levels** as compared to today(100-1000 times as of today), around **80 S-rich minerals** from Hadean period due to **volcanic activities**, total flux of intense **ultraviolet C (UVC) was 8 times greater than that at the present age.**
- ✓ The **natural solar-driven inorganic carbon conversion** emphasizes the important role of air-water interface coupling of minerals in fostering prebiotic biomolecules in the primitive Earth's environment.

Why this paper?

- ✓ The prebiotic **synthesis of formic acid (HCOOH)** occurs at the air-water aerosol microdroplet interface, facilitated by the presence of **metal sulfide** dust particles is done.
- ✓ This process significantly contributes to our understanding of the origin of life.
- ✓ It attempts to integrate all components to explain the origin of life in the **abiotic environment** of early Earth.

Background



SCIENCE ADVANCES | RESEARCH ARTICLE

GEOCHEMISTRY

Photoreduction of inorganic carbon(+IV) by elemental sulfur: Implications for prebiotic synthesis in terrestrial hot springs

Yanzhang Li[1,2]*, Yan Li[1,2]*†, Yi Liu[1,2], Yifu Wu[1,2], Junqi Wu[1,2], Bin Wang[3], Huan Ye[1,2], Haoning Jia[1,2], Xiao Wang[1,2], Linghui Li[1,2], Meixiang Zhu[1,2], Hongrui Ding[1,2], Yong Lai[1,2], Changqiu Wang[1,2], Jeffrey Dick[4], Anhuai Lu[1,2,4]†

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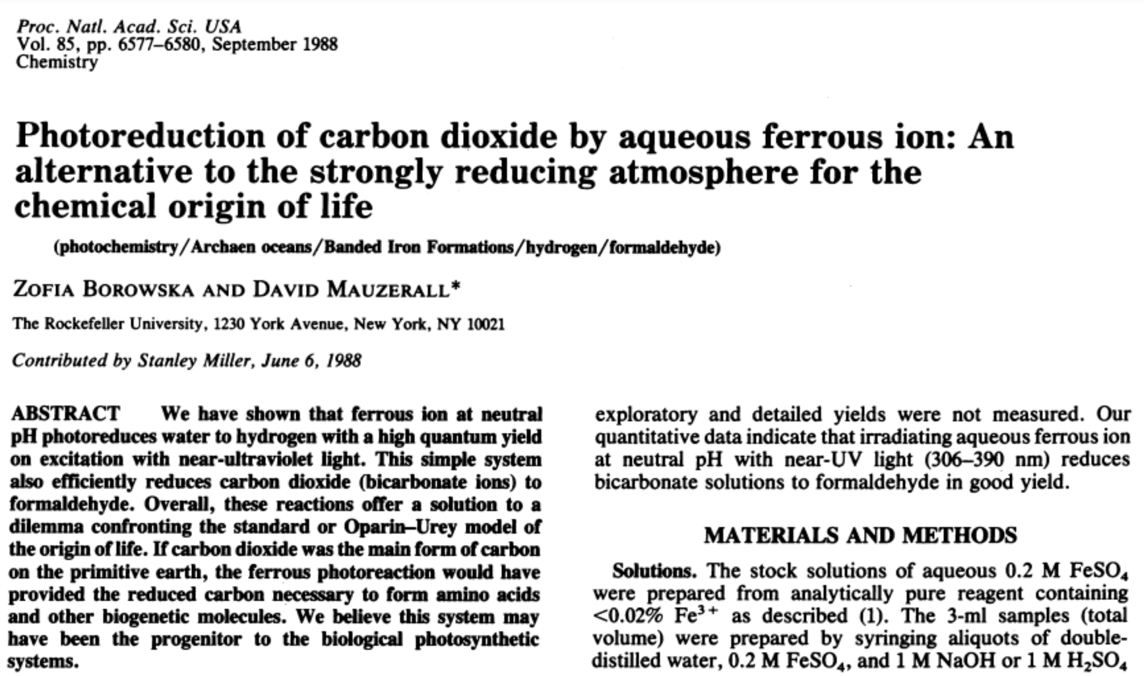
Terrestrial hydrothermal systems have been proposed as alternative birthplaces for early life but lacked reasonable scenarios for the supply of biomolecules. Here, we show that elemental sulfur (S^0), as the dominant mineral in terrestrial hot springs, can reduce carbon dioxide (CO_2) into formic acid (HCOOH) under ultraviolet (UV) light below 280 nm. The semiconducting S^0 is indicated to have a direct bandgap of 4.4 eV. The UV-excited S^0 produces photoelectrons with a highly negative potential of −2.34 V (versus NHE, pH 7), which could reduce CO_2 after accepting electrons from electron donors such as reducing sulfur species. Simultaneously, UV light breaks sulfur bonds, benefiting the adsorption of charged carbonates onto S^0 and assisting their photoreduction. Assuming that terrestrial hot springs covered 1% of primitive Earth's surface, S^0 at 10 μM could have produced maximal 10^9 kg/year HCOOH within 10-cm-thick photic zones, underlying its remarkable contributions to the accumulation of prebiotic biomolecules.



Proc. Natl. Acad. Sci. USA
Vol. 85, pp. 6577–6580, September 1988
Chemistry

Photoreduction of carbon dioxide by aqueous ferrous ion: An alternative to the strongly reducing atmosphere for the chemical origin of life

(photochemistry/Archaen oceans/Banded Iron Formations/hydrogen/formaldehyde)

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Contributed by Stanley Miller, June 6, 1988

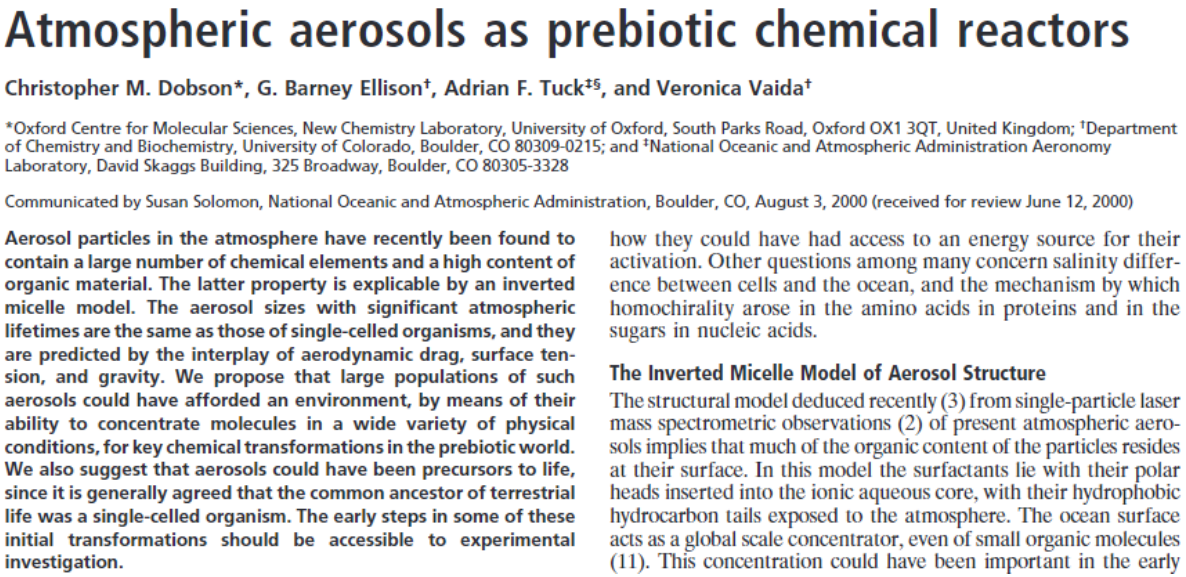
ABSTRACT **We have shown that ferrous ion at neutral pH photoreduces water to hydrogen with a high quantum yield on excitation with near-ultraviolet light. This simple system also efficiently reduces carbon dioxide (bicarbonate ions) to formaldehyde. Overall, these reactions offer a solution to a dilemma confronting the standard or Oparin–Urey model of the origin of life. If carbon dioxide was the main form of carbon on the primitive earth, the ferrous photoreaction would have provided the reduced carbon necessary to form amino acids and other biogenetic molecules. We believe this system may have been the progenitor to the biological photosynthetic systems.**

exploratory and detailed yields were not measured. Our quantitative data indicate that irradiating aqueous ferrous ion at neutral pH with near-UV light (306–390 nm) reduces bicarbonate solutions to formaldehyde in good yield.

MATERIALS AND METHODS

Solutions. The stock solutions of aqueous 0.2 M $FeSO_4$ were prepared from analytically pure reagent containing <0.02% Fe^{3+} as described (1). The 3-ml samples (total volume) were prepared by syringing aliquots of double-distilled water, 0.2 M $FeSO_4$, and 1 M NaOH or 1 M H_2SO_4

Background



Atmospheric aerosols as prebiotic chemical reactors

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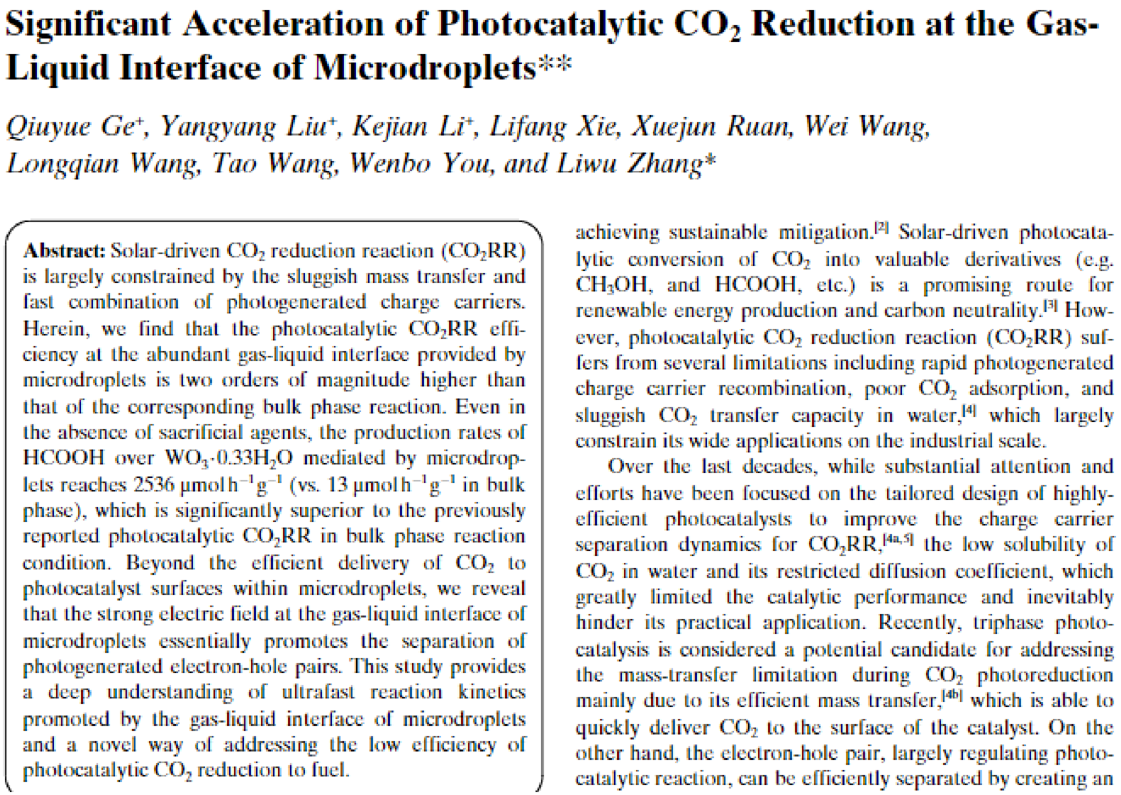
Communicated by Susan Solomon, National Oceanic and Atmospheric Administration, Boulder, CO, August 3, 2000 (received for review June 12, 2000)

Aerosol particles in the atmosphere have recently been found to contain a large number of chemical elements and a high content of organic material. The latter property is explicable by an inverted micelle model. The aerosol sizes with significant atmospheric lifetimes are the same as those of single-celled organisms, and they are predicted by the interplay of aerodynamic drag, surface tension, and gravity. We propose that large populations of such aerosols could have afforded an environment, by means of their ability to concentrate molecules in a wide variety of physical conditions, for key chemical transformations in the prebiotic world. We also suggest that aerosols could have been precursors to life, since it is generally agreed that the common ancestor of terrestrial life was a single-celled organism. The early steps in some of these initial transformations should be accessible to experimental investigation.

how they could have had access to an energy source for their activation. Other questions among many concern salinity difference between cells and the ocean, and the mechanism by which homochirality arose in the amino acids in proteins and in the sugars in nucleic acids.

The Inverted Micelle Model of Aerosol Structure

The structural model deduced recently (3) from single-particle laser mass spectrometric observations (2) of present atmospheric aerosols implies that much of the organic content of the particles resides at their surface. In this model the surfactants lie with their polar heads inserted into the ionic aqueous core, with their hydrophobic hydrocarbon tails exposed to the atmosphere. The ocean surface acts as a global scale concentrator, even of small organic molecules (11). This concentration could have been important in the early



Significant Acceleration of Photocatalytic CO$_2$ Reduction at the Gas-Liquid Interface of Microdroplets**

*Qiuyue Ge+, Yangyang Liu+, Kejian Li+, Lifang Xie, Xuejun Ruan, Wei Wang, Longqian Wang, Tao Wang, Wenbo You, and Liwu Zhang**

Abstract: Solar-driven CO$_2$ reduction reaction (CO$_2$RR) is largely constrained by the sluggish mass transfer and fast combination of photogenerated charge carriers. Herein, we find that the photocatalytic CO$_2$RR efficiency at the abundant gas-liquid interface provided by microdroplets is two orders of magnitude higher than that of the corresponding bulk phase reaction. Even in the absence of sacrificial agents, the production rates of HCOOH over WO$_3$·0.33H$_2$O mediated by microdroplets reaches 2536 μmol h^{-1} g^{-1} (vs. 13 μmol h^{-1} g^{-1} in bulk phase), which is significantly superior to the previously reported photocatalytic CO$_2$RR in bulk phase reaction condition. Beyond the efficient delivery of CO$_2$ to photocatalyst surfaces within microdroplets, we reveal that the strong electric field at the gas-liquid interface of microdroplets essentially promotes the separation of photogenerated electron-hole pairs. This study provides a deep understanding of ultrafast reaction kinetics promoted by the gas-liquid interface of microdroplets and a novel way of addressing the low efficiency of photocatalytic CO$_2$ reduction to fuel.

achieving sustainable mitigation.[2] Solar-driven photocatalytic conversion of CO$_2$ into valuable derivatives (e.g. CH$_3$OH, and HCOOH, etc.) is a promising route for renewable energy production and carbon neutrality.[3] However, photocatalytic CO$_2$ reduction reaction (CO$_2$RR) suffers from several limitations including rapid photogenerated charge carrier recombination, poor CO$_2$ adsorption, and sluggish CO$_2$ transfer capacity in water,[4] which largely constrain its wide applications on the industrial scale.

Over the last decades, while substantial attention and efforts have been focused on the tailored design of highly-efficient photocatalysts to improve the charge carrier separation dynamics for CO$_2$RR,[4a,5] the low solubility of CO$_2$ in water and its restricted diffusion coefficient, which greatly limited the catalytic performance and inevitably hinder its practical application. Recently, triphase photocatalysis is considered a potential candidate for addressing the mass-transfer limitation during CO$_2$ photoreduction mainly due to its efficient mass transfer,[4b] which is able to quickly deliver CO$_2$ to the surface of the catalyst. On the other hand, the electron-hole pair, largely regulating photocatalytic reaction, can be efficiently separated by creating an

Results and Discussion

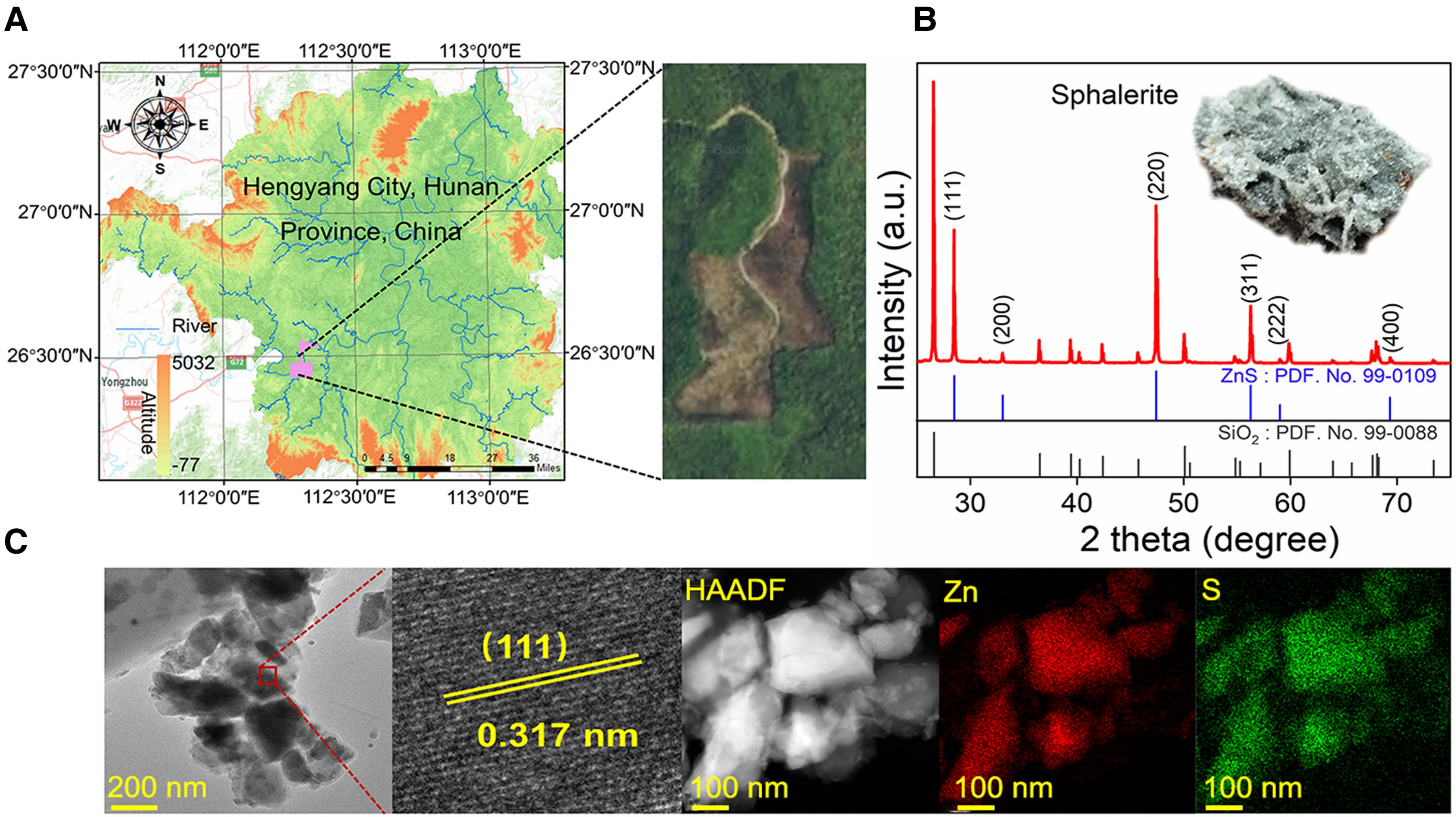
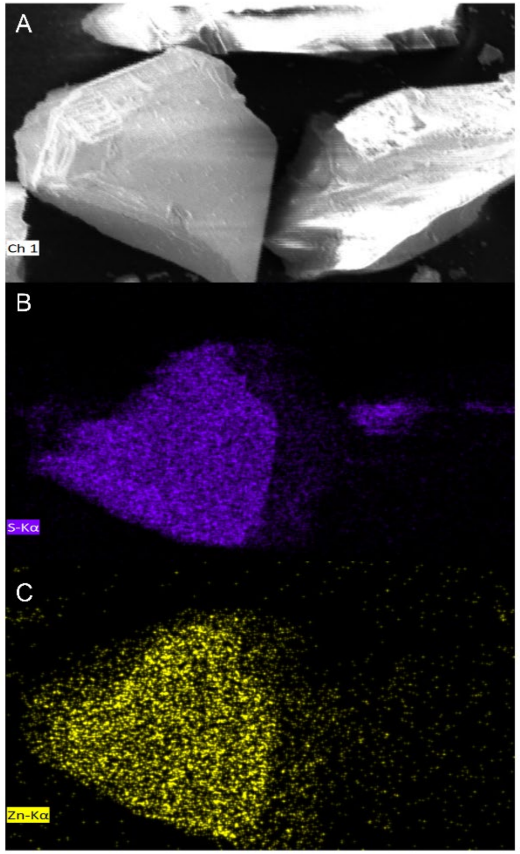


Fig. 1. Characterization of sphalerite. **A)** Geographic position of the natural sphalerite source. **B)** XRD pattern. **C)** Corresponding bright-field TEM, HAADF images, and EDS analysis for natural ZnS minerals.

Results and Discussion



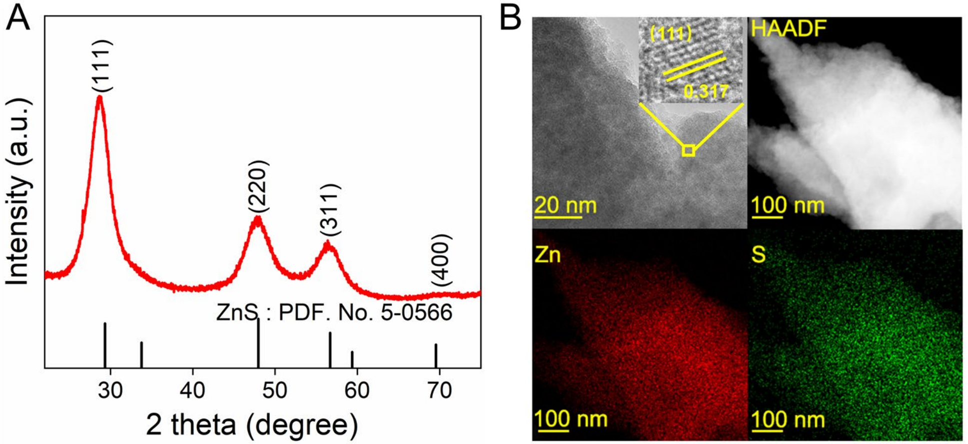


Figure S2. Characterization of **synthesized ZnS**. **(A)** XRD pattern of ZnS. **(B)**The corresponding bright-field TEM, HAADF-STEM, and EDS analysis of the compositional elements (HRTEM images, the lattice fringe is 0.317 nm corresponding to (111) crystal plane).

Figure S1. Scanning electron microscopy (SEM) of natural sphalerite mineral. **(A)** SEM image and EDS mapping of element **(B)** S, **(C)** Zn.

Results and Discussion

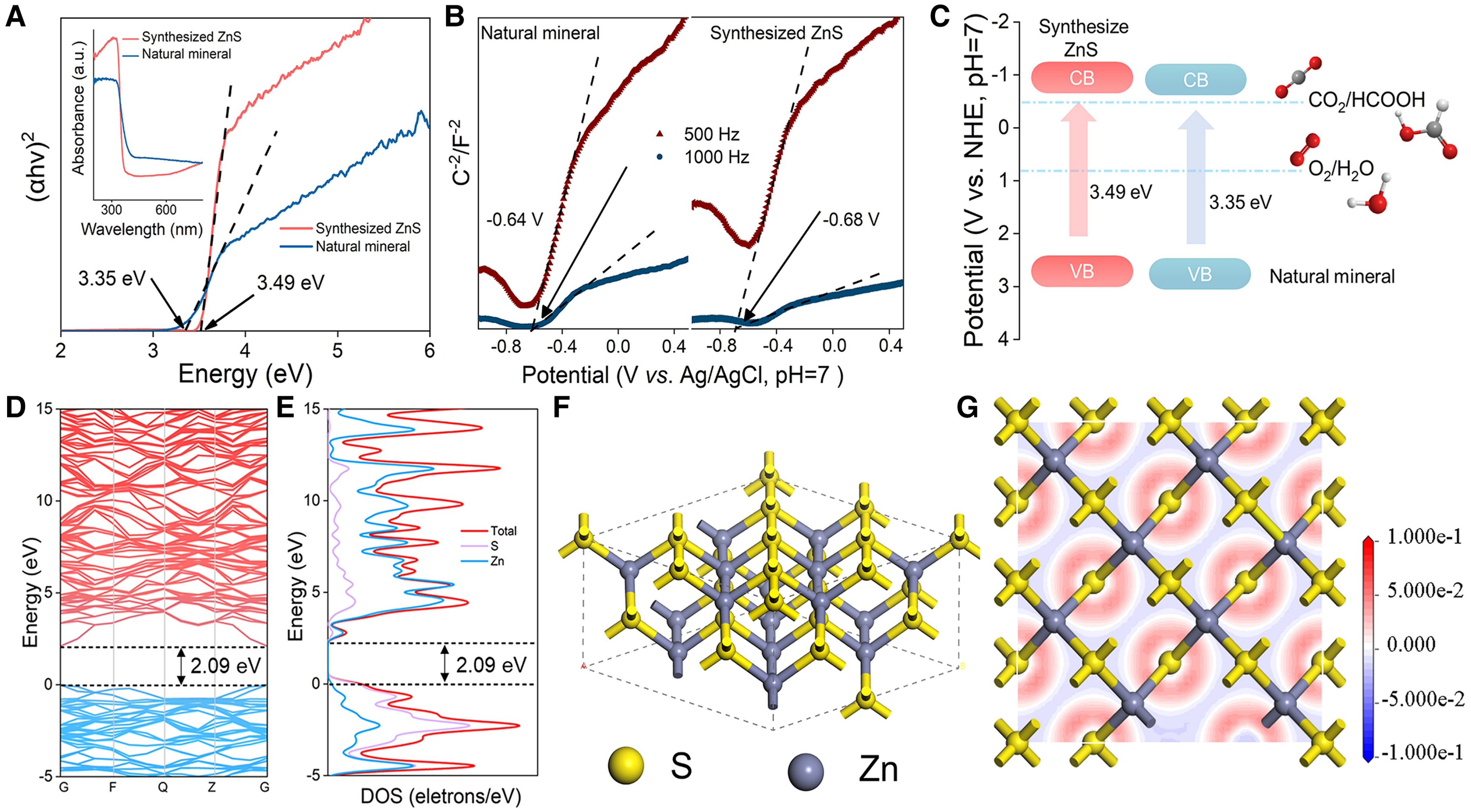


Fig. 2. Semiconducting properties and optical spectroscopy of ZnS. **A)** The obtained bandgaps of ZnS (inset: UV–Vis DRS). **B)** Mott–Schottky plots. **C)** Schematic illustration of the electronic band structures. **D)** Band structure. **E)** The DOSs. **F)** Overview of crystal structure. **G)** Electron density difference.

Results and Discussion

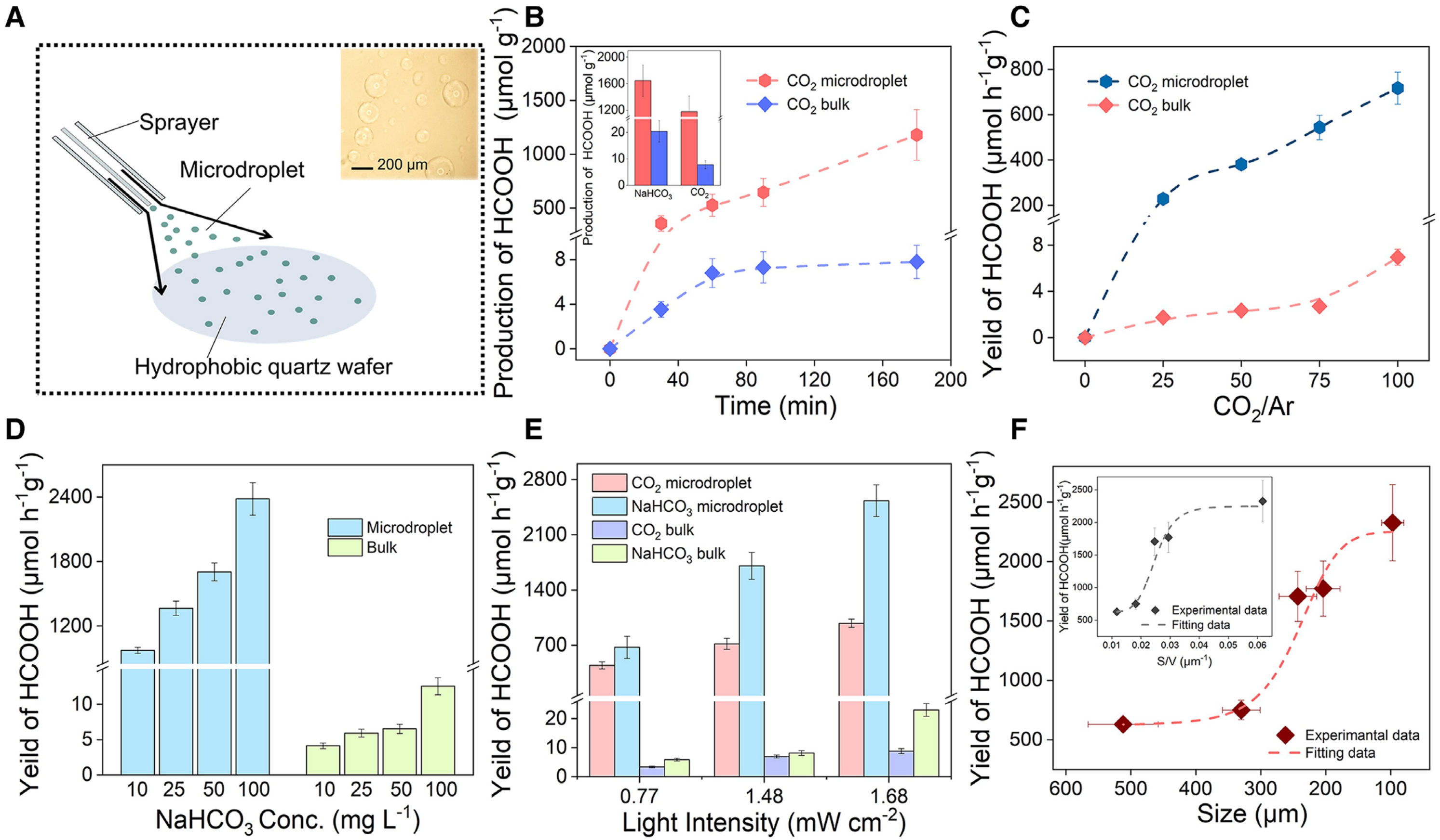


Fig. 3. The HCOOH production varied with the following conditions in the microdroplet reaction system. **A)** Schematic diagram of the microdroplets produced (inset: microscopic image of the produced microdroplets). **B)** Photoreduction inorganic carbon reaction under UV-lamp radiation (inset: the yield of HCOOH under different carbon sources after 180 min). The influences of **C)** CO_2 concentration (0, 25, 50, 100%), **D)** $NaHCO_3$ concentration on photoreduction reaction (10, 25, 50, and 100 mM; UV-lamp radiation; room temperature; 0.8 g L^{-1} ZnS), **E)** light irradiation intensity, and **F)** microdroplet size (inset: the correlation between the yield of HCOOH and the microdroplet S/V).

Results and Discussion

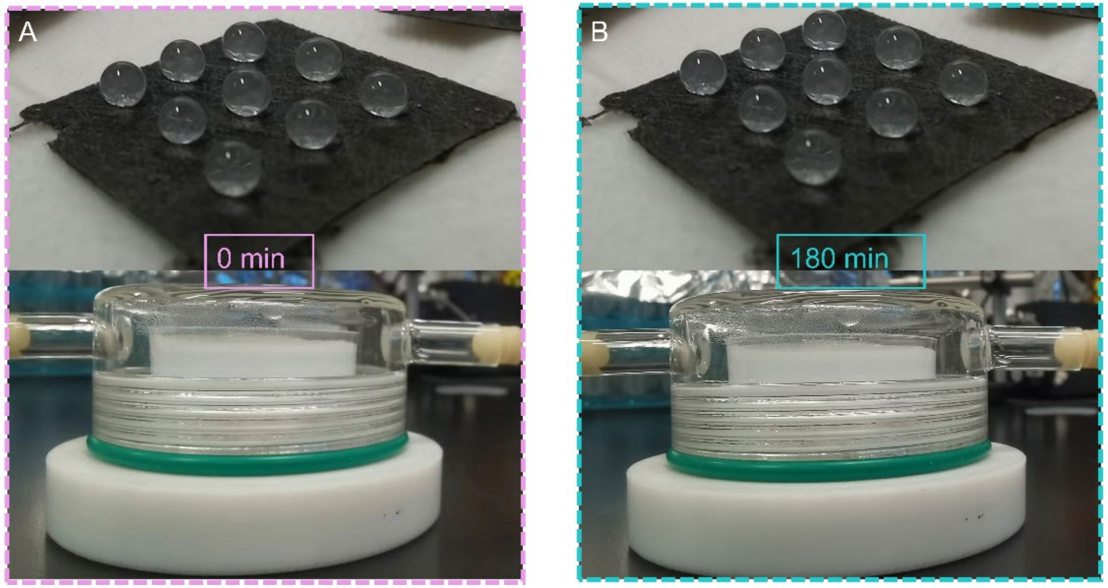


Figure S3. Images of microdroplets being stabilized at different time scales. The microdroplets were used to investigate the stability of the catalyst homogeneous dispersion in water microdroplets before **(A)** and after **(B)** 180 min.

Results and Discussion

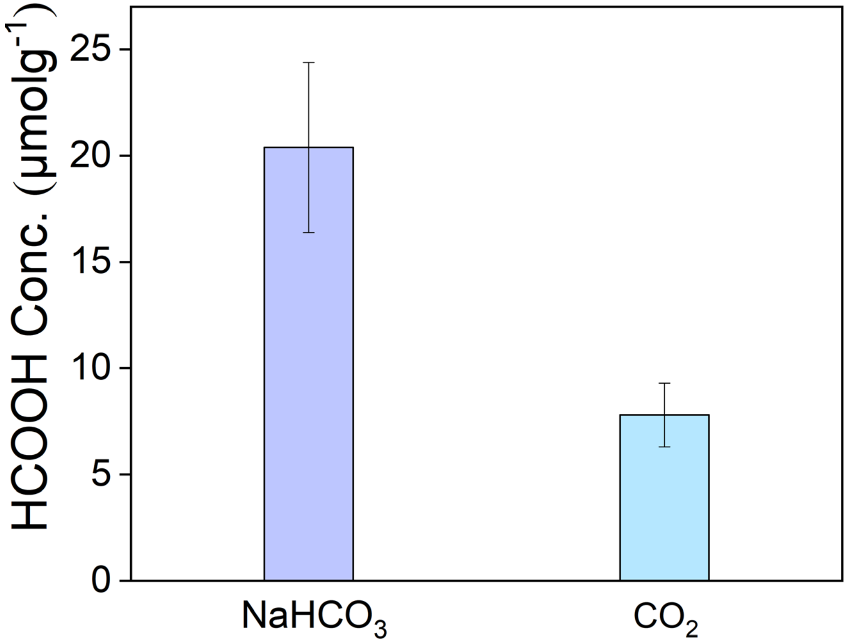


Figure S7. Bulk phase photoreduction inorganic carbon pre-experiment. Bulk phase reaction under different inorganic carbon sources. (310 nm UV lamp radiation, room temperature, 180 min, 0.8 g L^{-1} ZnS, 25 mM $NaHCO_3$).

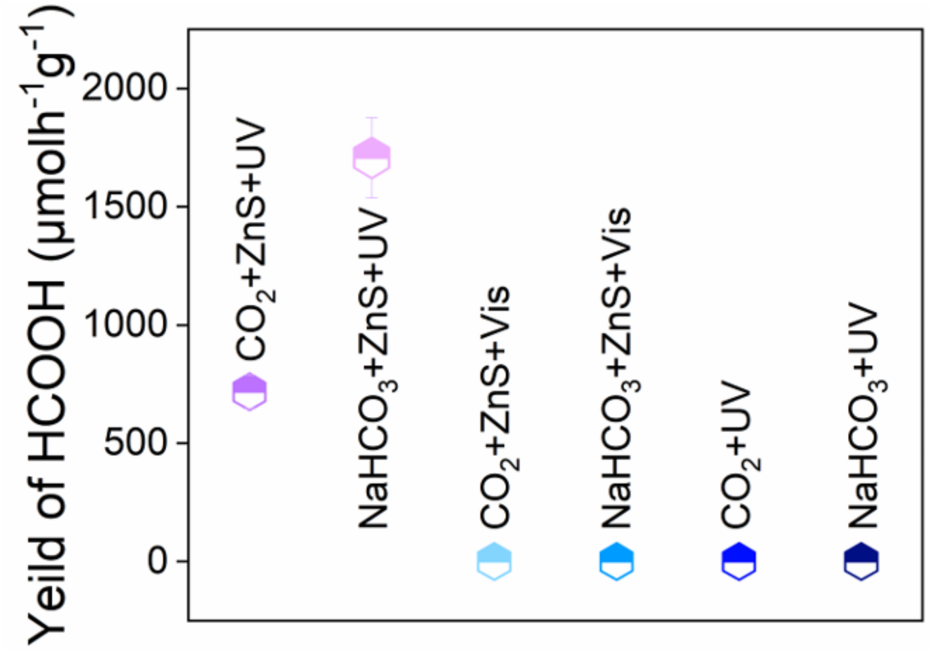


Figure S8. Control experiment of microdroplet system. Control experiment of microdroplet system under different conditions which were the absence of the ZnS, UV light radiation, and inorganic carbon source

Results and Discussion

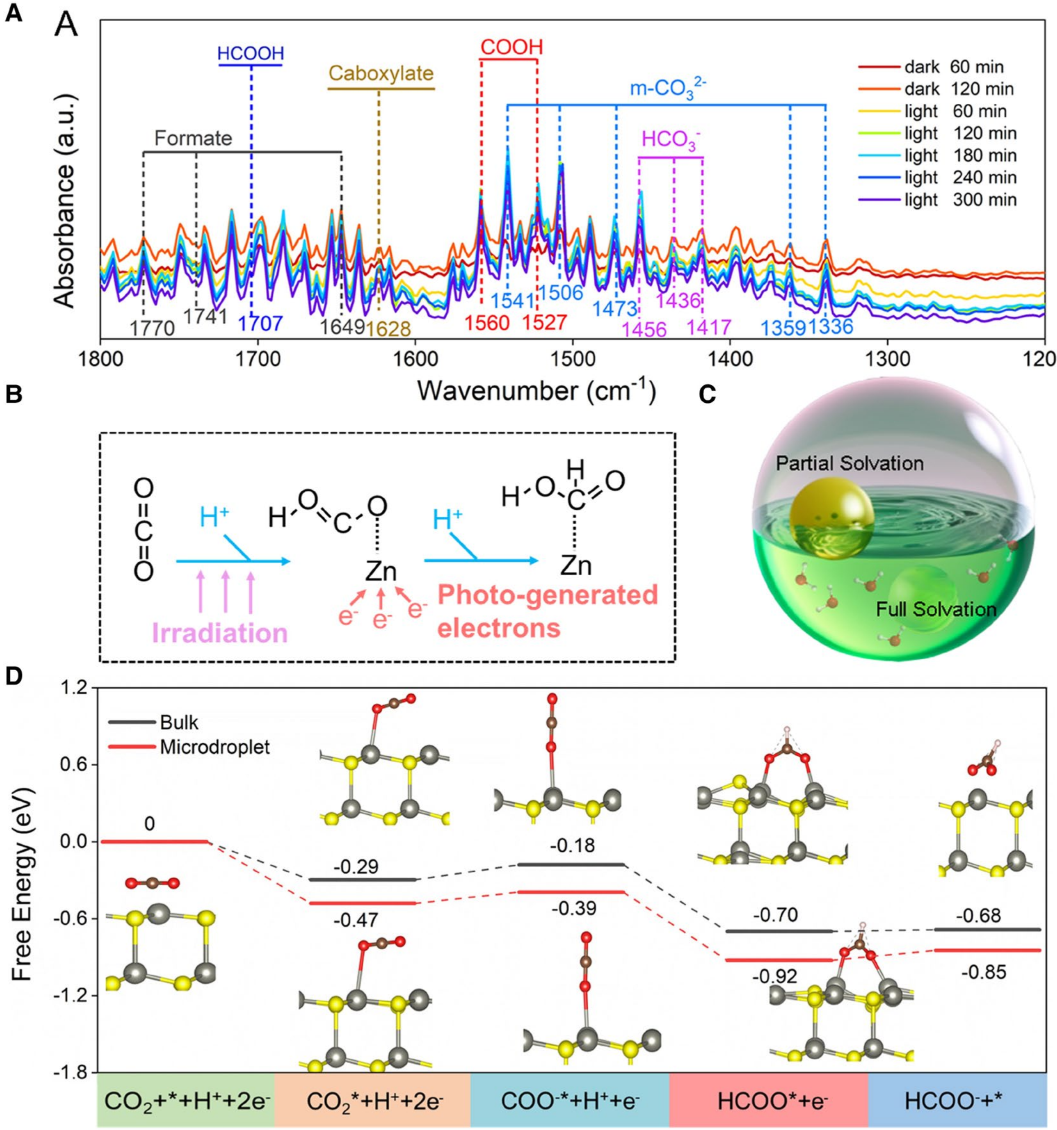


Fig. 4. ZnS-mediated inorganic carbon reduction pathways. **A)** In situ DRIFTS spectra for the photoreduction reaction. Diagrams of **B)** reaction pathway and **C)** partial solvation effect. **D)** Free energy diagram for the pathway of CO_2 conversion into HCOOH in microdroplet system and bulk phase reaction, indicating the electron/proton transfer process at the (001) surface of ZnS.

Results and Discussion

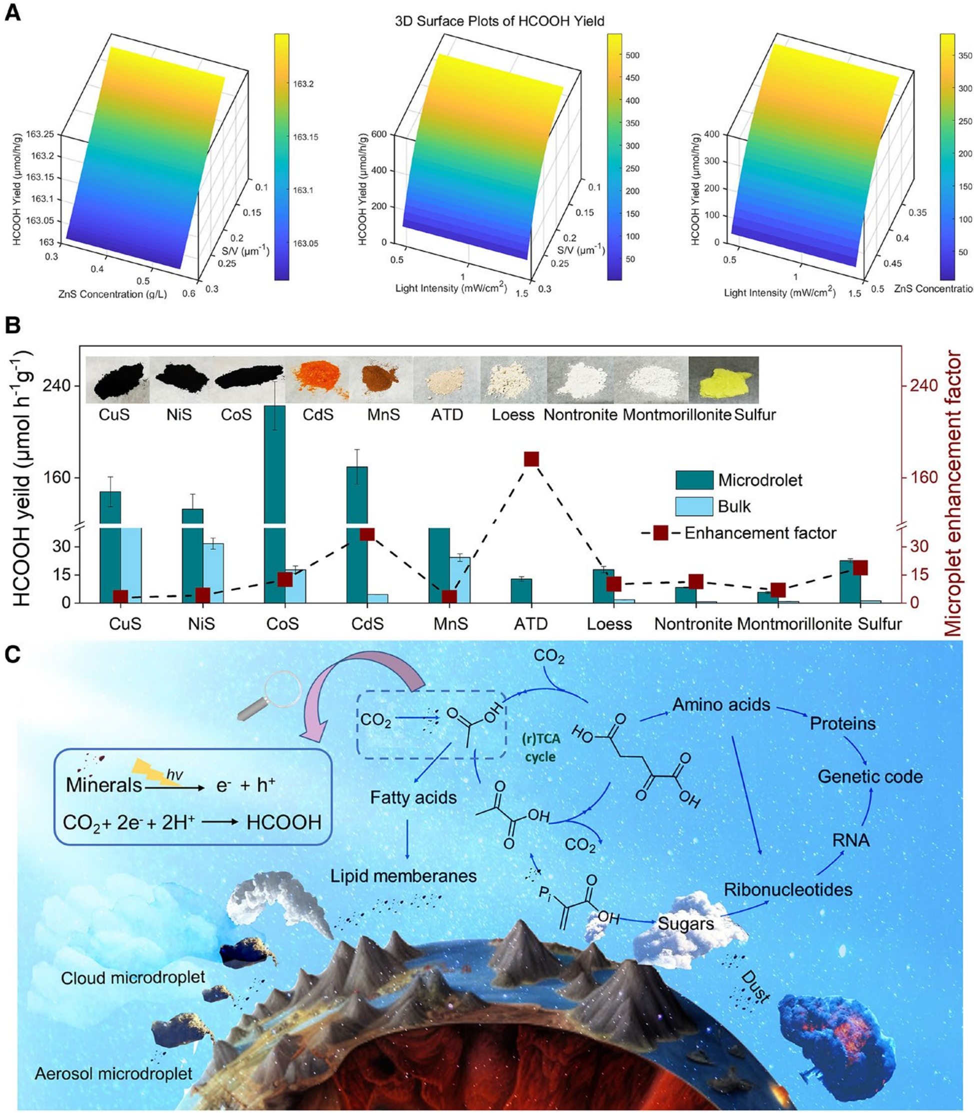


Fig. 5. Cumulative yields of HCOOH in the proposed model. **A)** The cumulative HCOOH depends on I (light intensity), SV (microdroplet S/V), and C_{ZnS} (concentration of ZnS). (50 mM carbonate ions, pH = 7, and 1.48 mW cm^{-2} UV wavelength was 310 nm.) **B)** Photoreduction CO_2 on various minerals within microdroplet. **C)** Schematic diagram of abiotic carbon fixation in the primitive Earth.

Results and Discussion

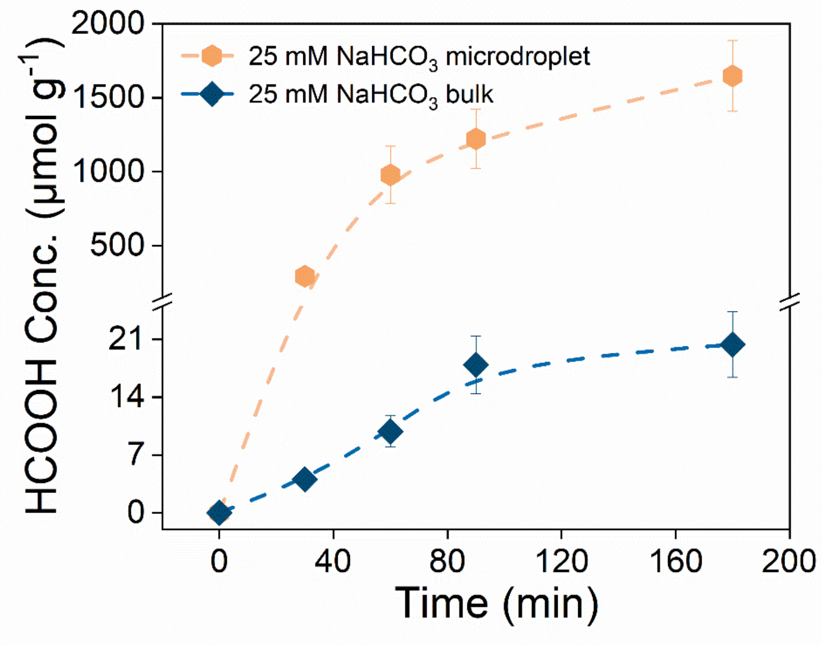


Figure S12. Time-dependence photocatalytic HCOOH production in $NaHCO_3$-system. The initial $NaHCO_3$ concentration is 25 mM both in bulk phase and microdroplet reaction. (UV lamp radiation, room temperature, 0.8 g L^{-1} ZnS).

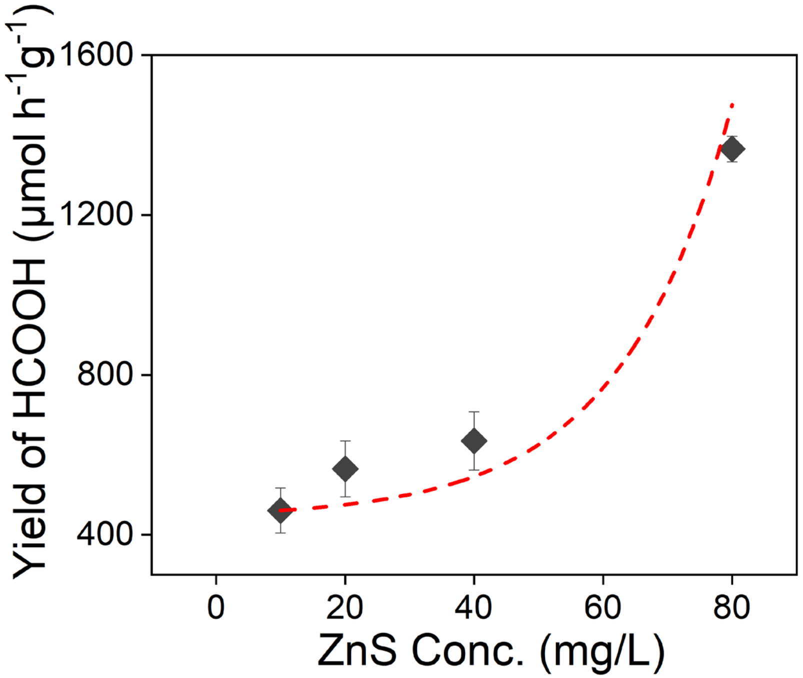


Figure S13. ZnS concentration-dependence photocatalytic HCOOH production in $NaHCO_3$-system. The initial $NaHCO_3$ concentration is 25 mM both in bulk phase and microdroplet reaction. (UV lamp radiation, room temperature,).

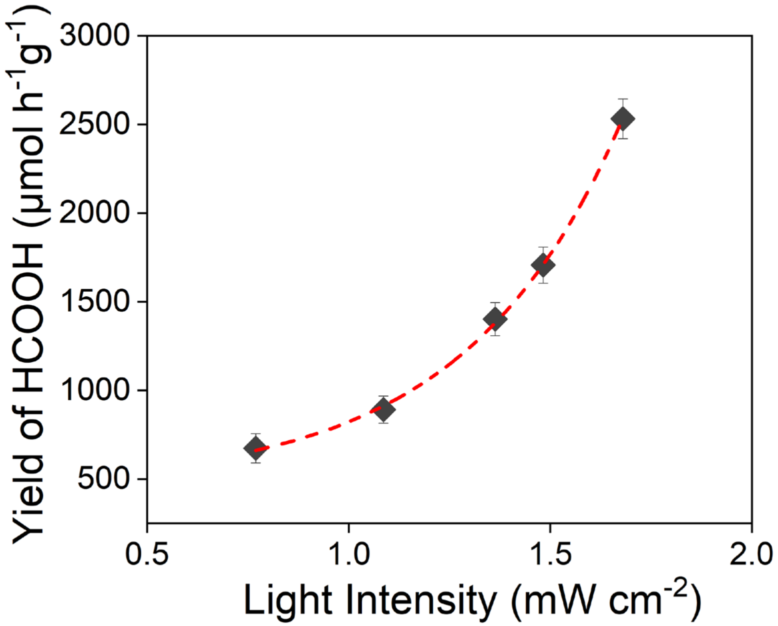


Figure S14. Light intensity-dependence photocatalytic HCOOH production in $NaHCO_3$-system. The initial $NaHCO_3$ concentration is 25 mM both in bulk phase and microdroplet reaction. (UV lamp radiation, room temperature,).

Conclusions

- ✓ The study of **metal sulfide minerals** suspended in airborne **aerosol microdroplets** significantly enhances our understanding of the origin of life.
- ✓ This process facilitates the **prebiotic synthesis of formic acid**, a crucial precursor that can lead to the formation of various biomolecules, which are the fundamental building blocks of life.
- ✓ It estimates the formic acid production to be **2.52×10^{14} Kg.year^{-1}.**
- ✓ To form formic acid, the involvement of all **UV light, metal sulfide minerals, and inorganic carbon** is essential.

–THANK YOU