Spontaneous generation of hydrogen peroxide from aqueous microdroplets

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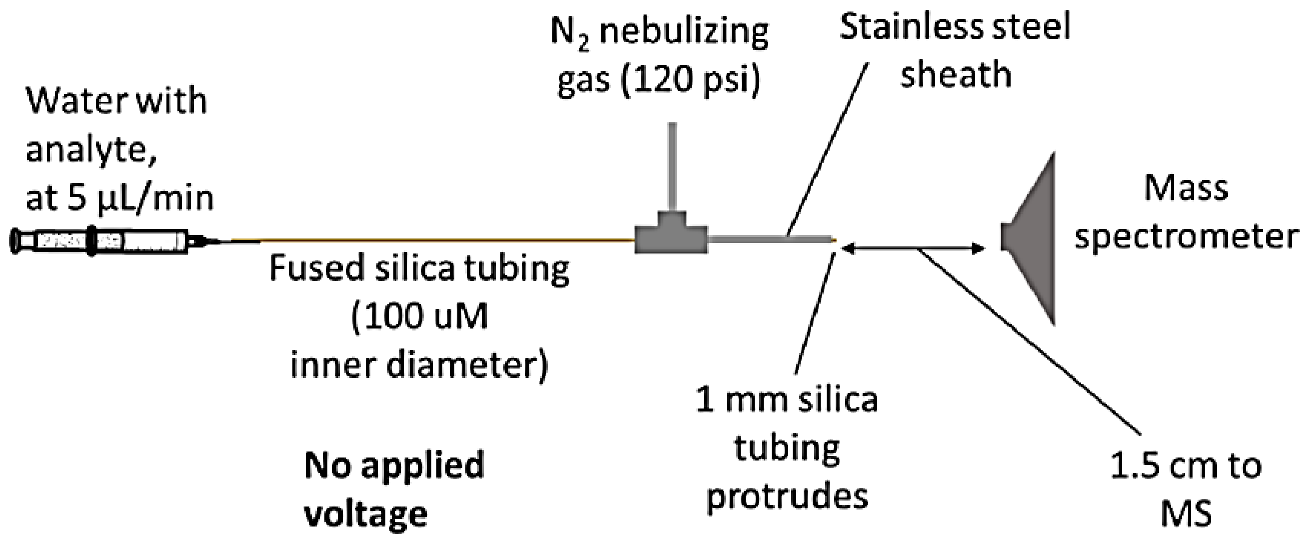

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Abiotic synthesis of purine and pyrimidine ribonucleosides in aqueous microdroplets

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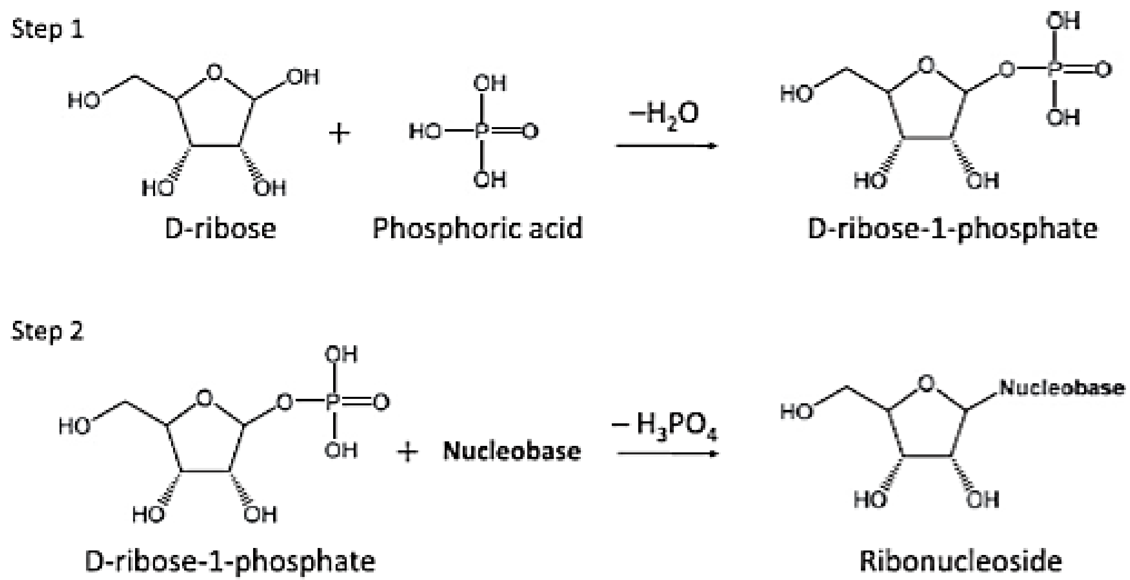

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Micrometer-Sized Water Droplets Induce Spontaneous Reduction

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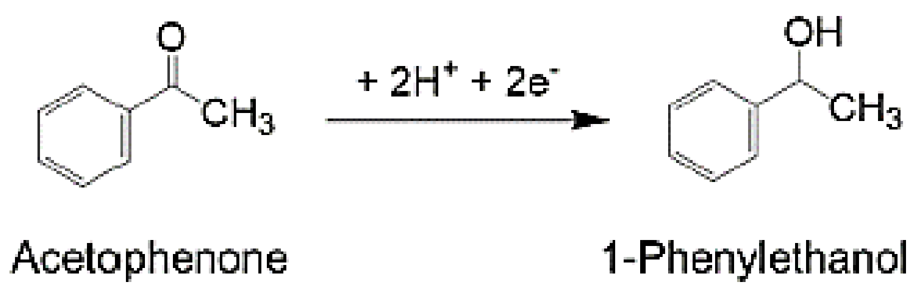
Microdroplets provide a new foundation for green chemistry by rendering water molecules to be highly electrochemically active without any added reducing agent or applied potential.



Significance of the work

- Water is considered to be a stable and relatively inert molecule in bulk solution.

- Exceptional behaviour of water: Water molecules are spontaneously oxidized to form hydrogen peroxide near the water−air interface of micron-sized water droplets.

- This process does not require any chemical reagent catalyst, applied electric potential, or radiation. Only pure water in the form of microdroplets in air is necessary for the appearance of hydrogen peroxide.

- This discovery opens various innovative opportunities including green and inexpensive production of hydrogen peroxide, green chemical synthesis, safe cleaning, and food processing.

Introduction

- H_2O_2 is spontaneously produced from pure water by atomizing bulk water into microdroplets (1 µm to 20 µm in diameter).
- Production of H_2O_2, as assayed by H_2O_2-sensitve fluorescence dye peroxyfluor-1, increased with decreasing microdroplet size.
- The generated H_2O_2 concentration was ∼30 µM as determined by titration with potassium titanium oxalate.
- Changing the spray gas to O_2 or bubbling O_2 decreased the yield of H_2O_2 in microdroplets, indicating that pure water microdroplets directly generate H_2O_2 without help from O_2 either in air surrounding the droplet or dissolved in water.
- Out of several mechanism studies, it is evident that hydroxyl radical (OH) recombination is the most likely source, in which OH is generated by loss of an electron from OH^- at or near the surface of the water microdroplet.
- This catalyst free and voltage-free H_2O_2 production method provides innovative opportunities for green production of hydrogen peroxide

H_2O_2 generation in microdroplet probed by a H_2O_2- sensitive fluorescence probe

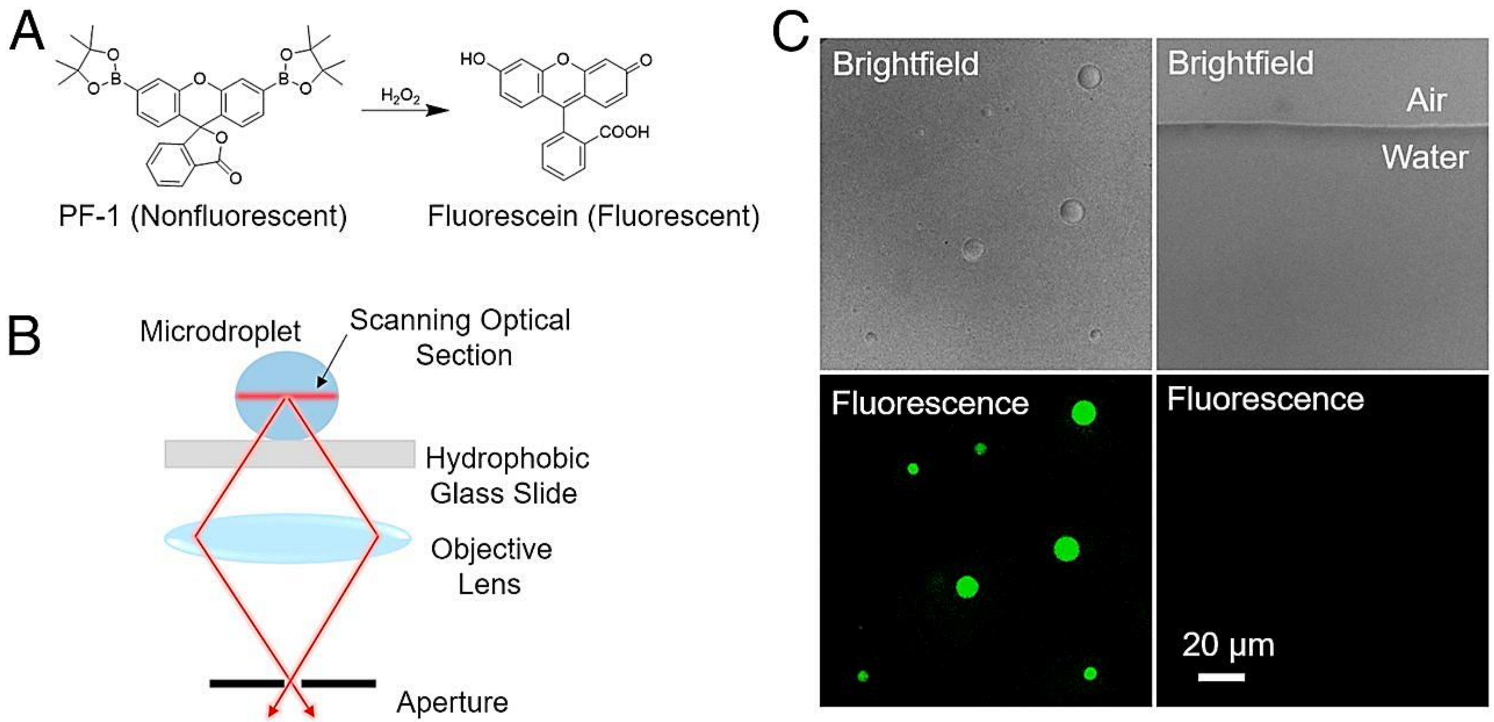


Fig. 1. Fluorescence imaging of spontaneous generation of hydrogen peroxide in aqueous microdroplets: (A) reaction scheme between PF-1 and hydrogen peroxide; (B) schematic of confocal microscope setup for imaging microdroplets; and (C) brightfield and fluorescence images of microdroplets (2 μm to 17 μm in diameter) at Left and bulk water at Right including the flat air-bulk-water interface. Each sample contains 10 μM PF-1. Only microdroplets display fluorescence from fluorescein caused by H_2O_2 cleavage of PF-1. (Scale bar, 20 μm.)

H_2O_2 generation in microdroplet probed by a H_2O_2- sensitive fluorescence probe

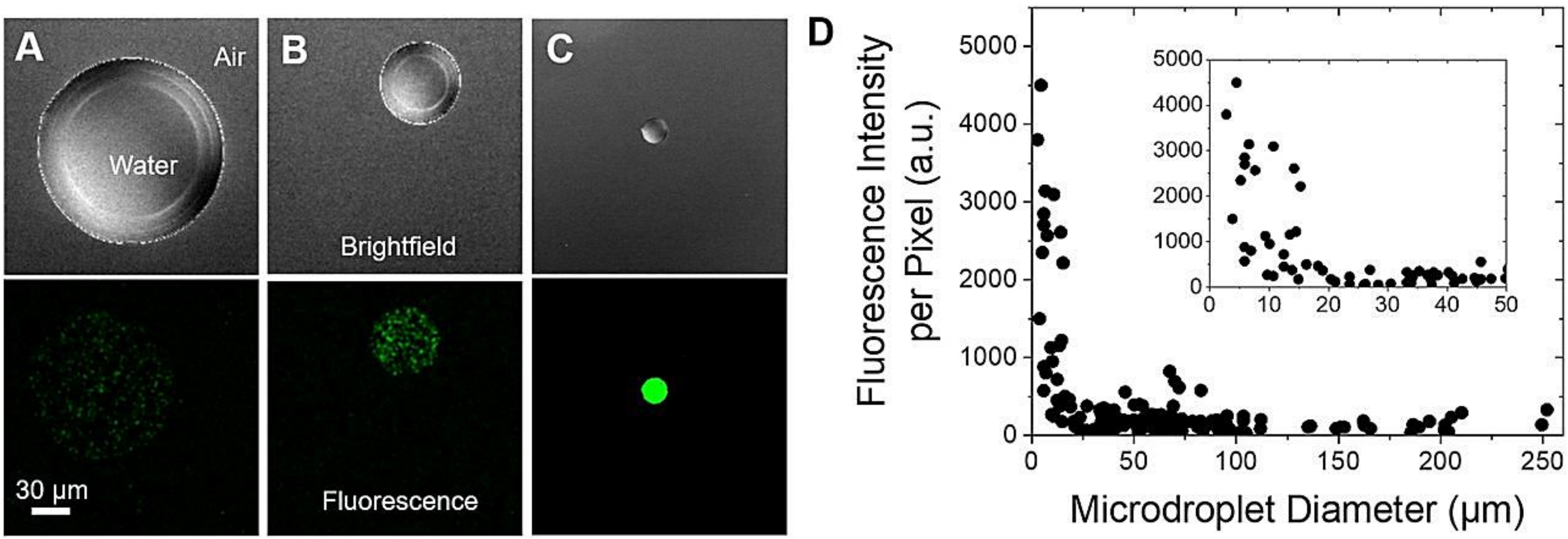


Fig. 2. Dependence of fluorescence intensity on the size of microdroplets. Brightfield and fluorescence images of microdroplets containing 10 µM PF-1 with diameters of (A) 160 µm, (B) 50 µm, and (C) 16 µm. (D) Relationship between fluorescence intensity and microdroplet diameter, indicating a higher concentration of hydrogen peroxide is generated in smaller microdroplets. (Inset) fluorescence intensity vs. microdroplet diameter for 1 µm to 50 µm. (Scale bar, 30 µm.)

H_2O_2 generation in microdroplet using mass spectrometry and NMR

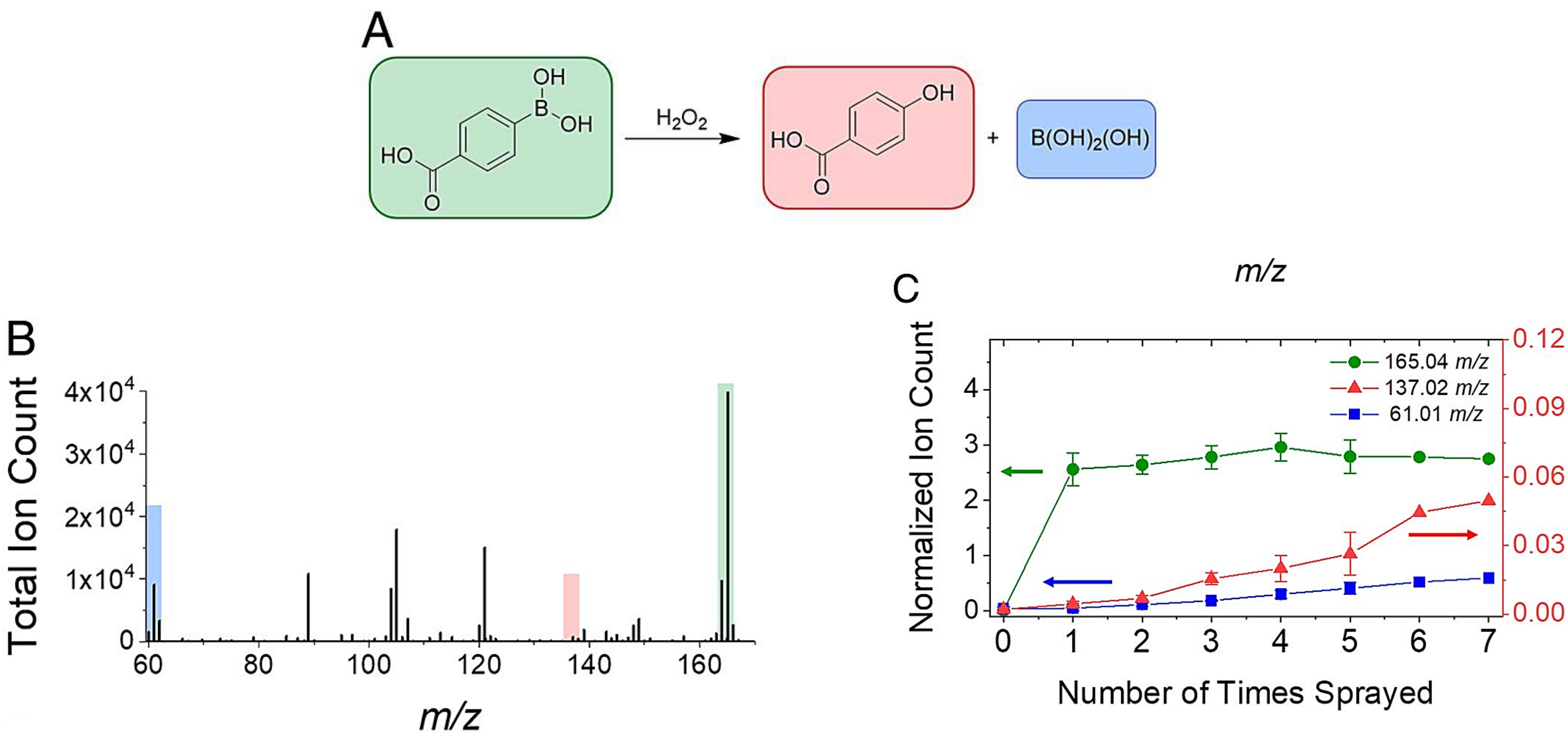


Fig. 3. Molecular signature of H_2O_2 production in aqueous microdroplets using boronic acid probe as a function of consecutive sprays. (A) Reaction scheme of H_2O_2-promoted deborylation of 4-CPB. (B) Mass spectrum of aqueous microdroplets containing 100 µM 4-CPB and 10 µM sodium benzoate (as internal standard) on the seventh consecutive spray. (C) Normalized ion count of 4-CPB (purple, 165 m/z) starting material, and H_2O_2 deborylation products, 4-HB acid (red, 137 m/z) and boric acid (blue, 61 m/z), over multiple sprays. Error bars represent 3 replicates for sprays 1 through 4, and 2 replicates for spray 5.

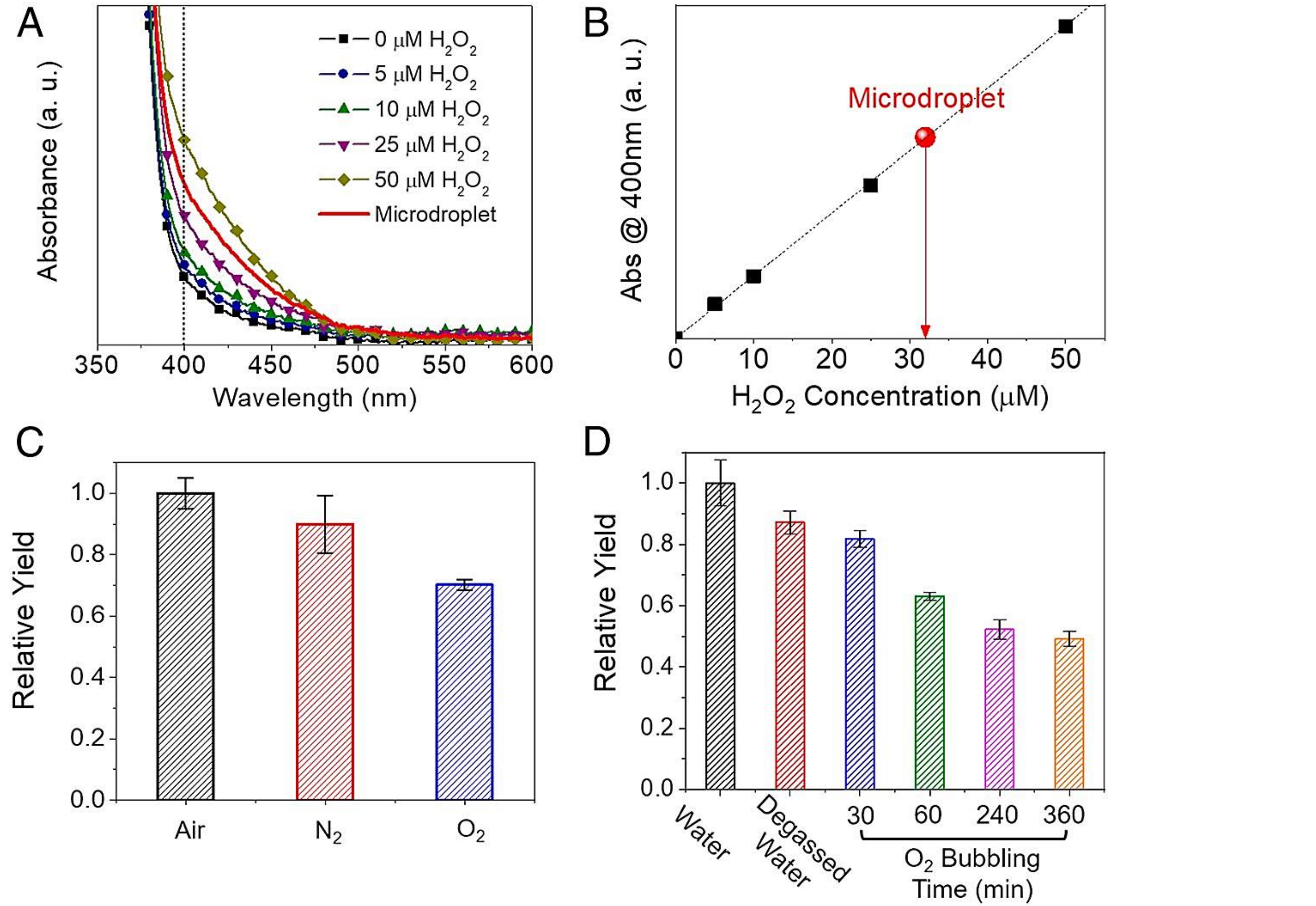


Fig. 4. H_2O_2 concentration as a function of different operating conditions. (A) Absorption spectrum of aqueous PTO solution with added H_2O_2. Example microdroplet spectrum in red. (B) Calibration curve at 400 nm from A. The red circle represents the concentration of H_2O_2 generated from aqueous microdroplets acquired from the spectra in A.
(C) The effect of varying the nebulizing gas. (D) The effect of dissolving different gases in water. Both C and D are measured with peroxide test strips. Error bars represent 1 SD from 3 measurements.

Mechanism of H_2O_2 generation in microdroplet

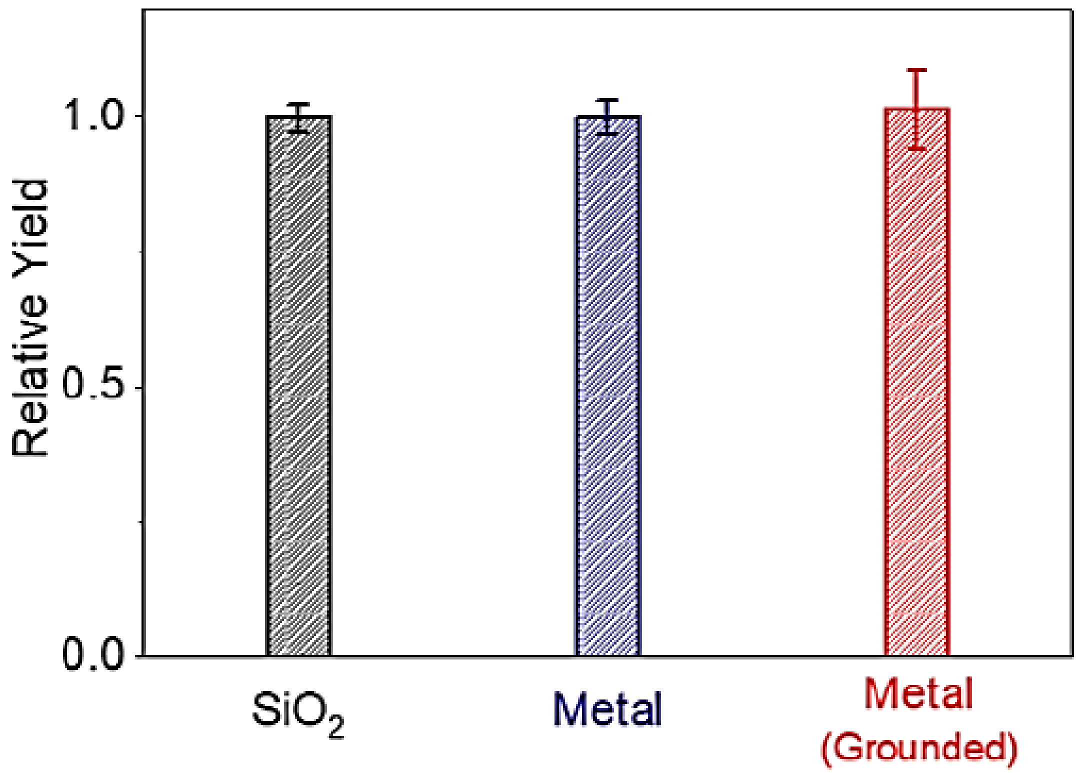


Fig: The relative production yield of H_2O_2 with different capillary materials including fused silica and stainless steel metal. The effect of grounding (0 V) on the H_2O_2 production yield was also measured

Possible origins for the formation of H_2O_2
1. Triboelectric effect 2. Asymmetric charge separation during fission
3. Electrification 4. oxidation of water by intrinsic surface potential of water-microdroplet surface

Mechanism of H_2O_2 generation in microdroplet

At air-water interface

$$H_2O \longrightarrow H^+ + OH^-$$

$$OH^- \xrightarrow{\vec{E},\ \Delta pH} OH^\bullet + e^-(solv)$$

$$OH^\bullet + OH^\bullet \longrightarrow H_2O_2$$

- autoionization of water
- Formation of OH radicals
  release of a solvated electron
- Recombination of OH radicals

Fig. 5. Proposed mechanism to form H_2O_2 at the air−water interface of microdroplets

Conclusions

- The present work establishes the spontaneous generation of H_2O_2 from aqueous microdroplets and offers a method for its direct production from water.
- This chemical free, catalyst-free, and voltage-free synthesis of H_2O_2 needs only water and modest equipment to generate sprayed microdroplets.
- Although water is a most common substance, its behaviour still holds many poorly understood features.
- The present study on water microdroplets emphasizes how different their behaviour can be from bulk water