Supplementary Information

Electrodeless Hydrogen Production from Seawater Using Femtosecond Laser Pulses

Akira Kuwahara,*[a,†] Yuki Mizushima,*[b,†] Makoto Matsui,[b,c] Tomoki Kozuka[d] and Nobuyuki Mase[c,d]

[a] *Department of Applied Energy, Nagoya University, Aichi 464-8603, Japan*

[b] *Department of Mechanical Engineering, Shizuoka University, Shizuoka 432-8561, Japan*

[c] *Green Energy Research Division, Research Institute of Green Science and Technology, Shizuoka University, Shizuoka 432-8561, Japan*

[d] *Department of Engineering, Shizuoka University, Shizuoka 432-8561, Japan*

[†] *These authors contributed equally.*

* Corresponding authors. Email: akuwahara@energy.nagoya-u.ac.jp (Akira Kuwahara); Email: mizushima.yuhki@shizuoka.ac.jp (Yuki Mizushima)

Sample materials

Artificial seawater (MARINE ART SF-1, Tomita Pharmaceutical) was used as seawater sample. Its nutritional information is listed in Table S1.

Hydrogen analysis

The analysis procedure and experimental apparatus are displayed in Fig. 1. A typical chromatogram observed in the gas chromatograph and calibration line is shown in Fig. S1.

Gas composition analysis using a quadrupole mass spectrometer

We carried out gas composition analyses of two gas samples generated from ultrapure water and seawater to confirm the generation of toxic gases. A gas chromatograph (GCMS-QP2010 Ultra, Shimadzu) with a quadrupole mass spectrometer was used. The liquid samples in cells were irradiated with femtosecond laser beams at a repetition frequency of 1 kHz for about three hours. To prevent the dissolution of the generated gas into the residual liquid after irradiation, the liquid was drained by the internal pressure during irradiation. Note that the irradiation conditions, for example, the irradiation time, internal pressure in the cell, were different from the experiments shown in Fig. 2 and Fig. 3.

Mass spectra of gas samples generated from ultrapure water and seawater are shown in Fig. S2, and the gas compositions generated by laser radiation are listed in Table S2. In both samples, the main components were H_2 (m/z = 2) and O_2 (m/z = 16), and the generation of Cl_2 gas was not observed, where the limit of detection was estimated to be approximately 1 nL using CO_2 (m/z = 44) as a reference.

In the gas produced from seawater, 4.6 nL hydrochloric acid HCl (m/z = 36) gas was detected, and the concentration was estimated to be approximately 7.3 ppm. Here the amounts of contaminated species (N_2, O_2, Ar, CO_2 in air) were eliminated by using the total amount of N_2 as an indicator.

Experimental results of the reproductive experiment

We performed the reproductive experiment using a standard rectangular cell (F15-UV-10, GL Science) with a screw cap and PTFE silicone septum. The comparison of experimental conditions is listed in Table S3. The amount of hydrogen generation from ultrapure water is shown in Fig. 2(a), and our experiment is in good agreement with the previous result, where the production rate of 20 μmol h^{-1} estimated from the linear fitting was used [1]. Therefore, the curvature of a cylindrical cell can cause H_2 production enhancement owing to the increase in the energy density associated with light focus.

Pressure measurement

The inner pressure in a cell was monitored by using a specialized cell (SX-10, Agri) and a gauge pressure sensor (AP-C30, Keyence). A joint was attached to the end of the branch pipe and connected to the pressure sensor.

Light efficiency evaluation

To evaluate the light efficiency, the transmittance of the incident laser beam was measured by using a power meter (10A-V1.1, Ophir). The experimental apparatus is shown in Fig. S3. The light efficiency includes absorption by a cell window. Table S4 shows the light efficiencies in ultrapure water, seawater, and 2.5 times concentrated seawater.

Table S1 Nutritional information of artificial seawater

Chemical species	Salt weight per liter
NaCl	22.1 g
$MgCl_2$ $6H_2O$	9.9 g
$CaCl_2$ $2H_2O$	1.5 g
Na_2SO_4	3.9 g
KCl	0.61 g
$NaHCO_3$	0.19 g
KBr	96 mg
$Na_2B_4O_7$ $10H_2O$	78 mg
$SrCl_2$	13 mg
NaF	3 mg
LiCl	1 mg
KI	81 μg
$MnCl_2$ $4H_2O$	0.6 μg
$CoCl_2$ $6H_2O$	2 μg
$AlCl_3$ $6H_2O$	8 μg
$FeCl_3$ $6H_2O$	5 μg
Na_2WO_4 $2H_2O$	2 μg
$(NH_4)_6Mo_7O_{24}$ $4H_2O$	18 μg

Table S2 Gas composition

Species (*m/z*)	Ultrapure water	Seawater
H_2 (*m/z* = 2)	7.7×10^{-1}	5.9×10^{-1}
O_2 (*m/z* = 16)	2.3×10^{-1}	4.1×10^{-1}
HCl (*m/z* = 36)	Not detected*	7.3×10^{-6}

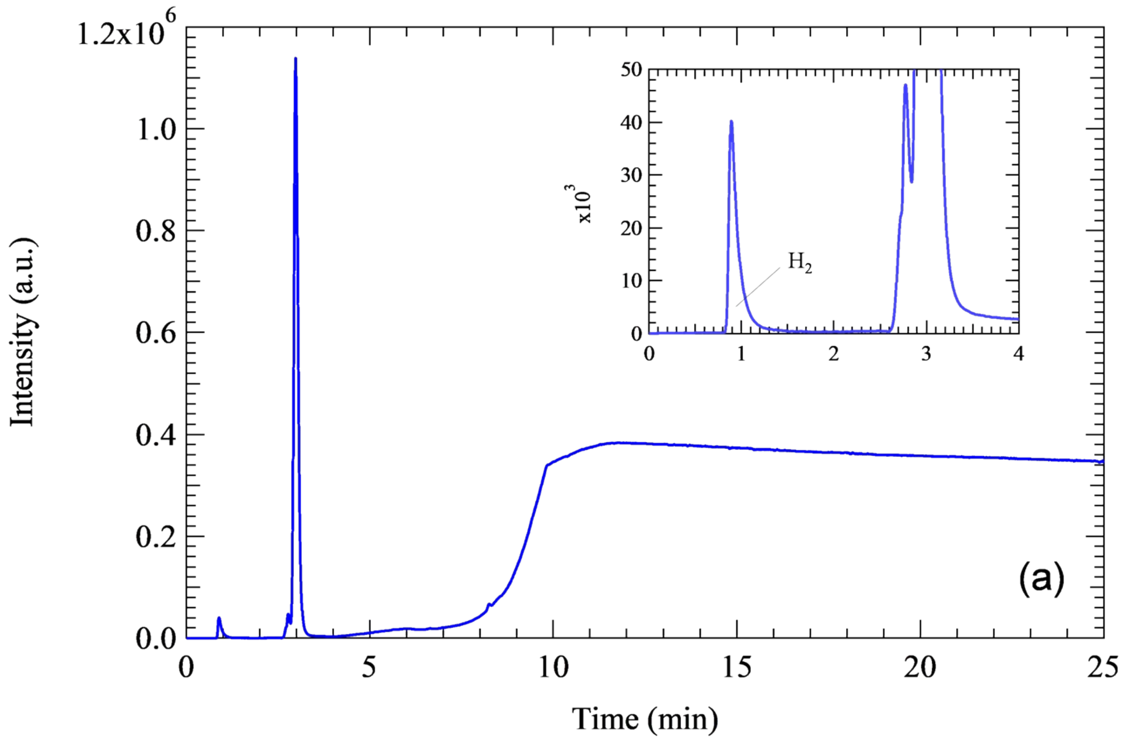
* The limit of detection is approximately 1 nL, and the corresponding concentration is 1.6 ppb in the seawater sample.

Table S3 Comparison of typical experimental conditions

Parameters	This study	The previous study
Wavelength	810 nm	800 nm
Pulse width	120 fs	100 fs
NA of an objective lens	0.28	0.25
Cell	F15-UV-10 (GL Science)	F15-UV-10 (GL Science)
Sample	Ultrapure water	Ultrapure water

Table S4 Light efficiency evaluation

Sample	Light efficiency (%)
Ultrapure water	46
Seawater	49
2.5 times concentrated seawater	55



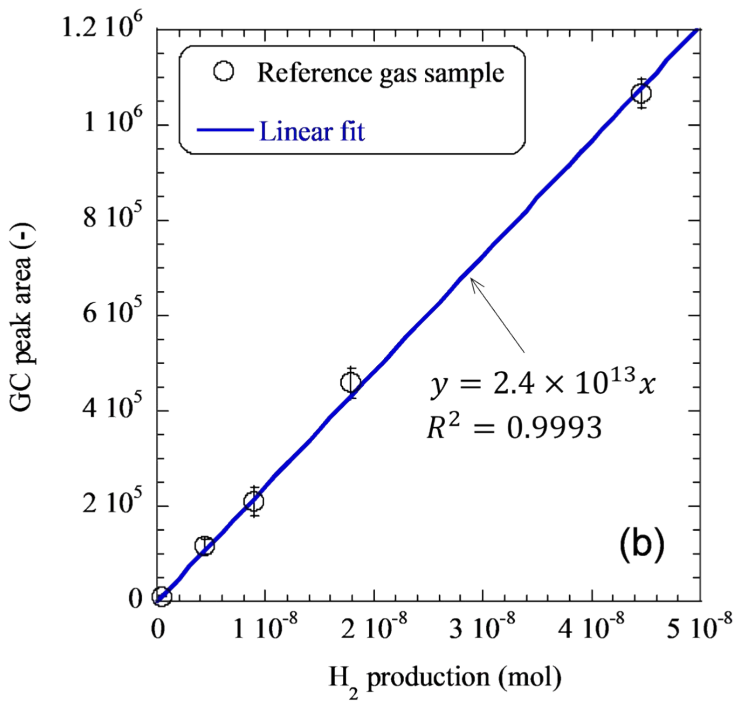
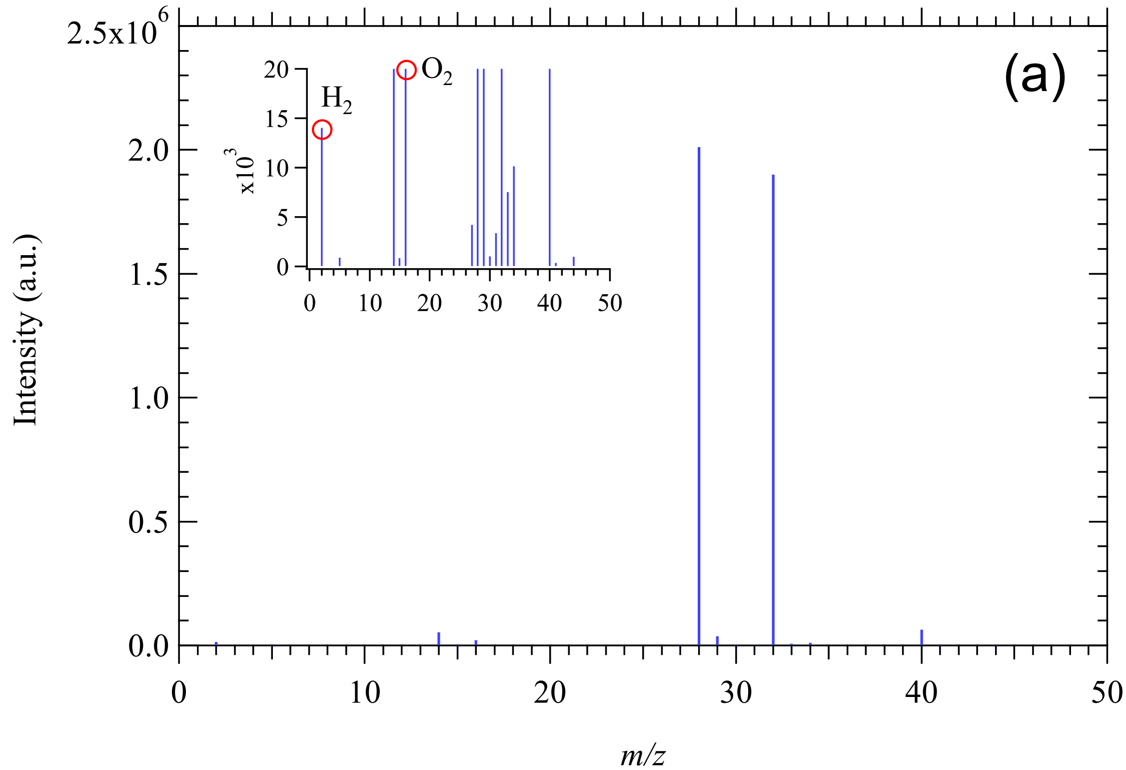


Fig. S1. (a) Chromatogram obtained by a gas chromatograph. **(b)** Calibration line of H_2 gas.



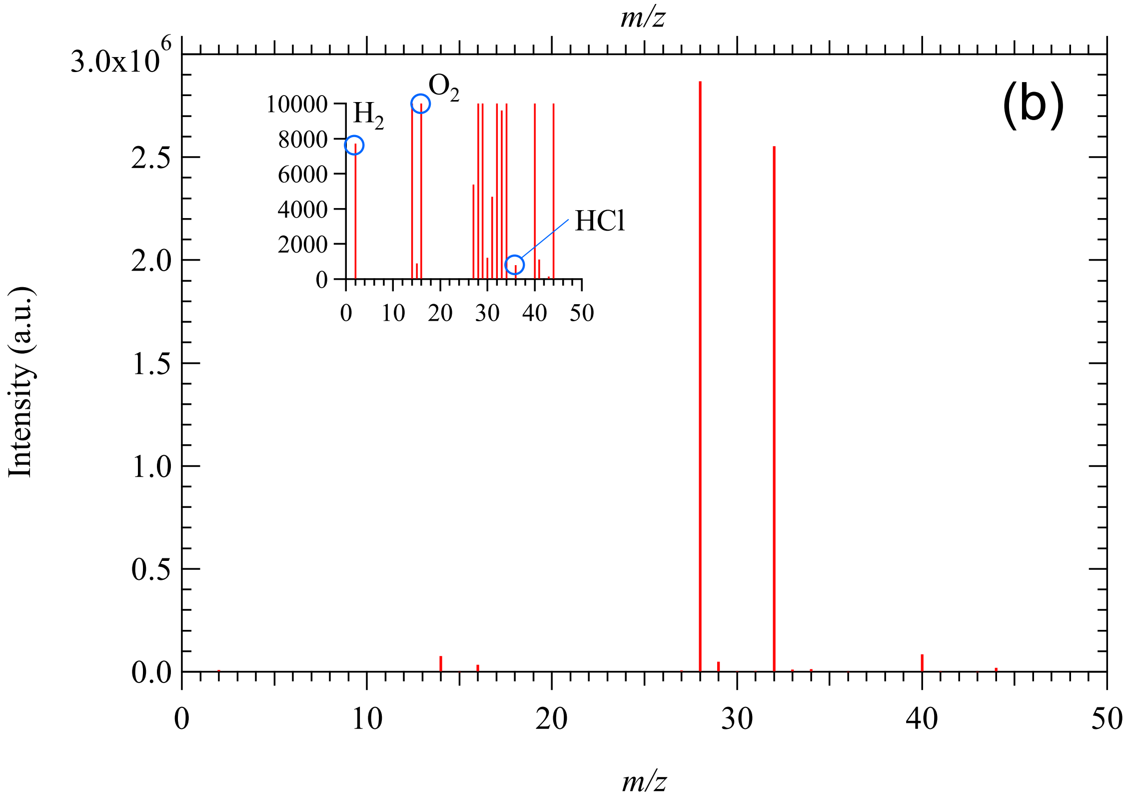
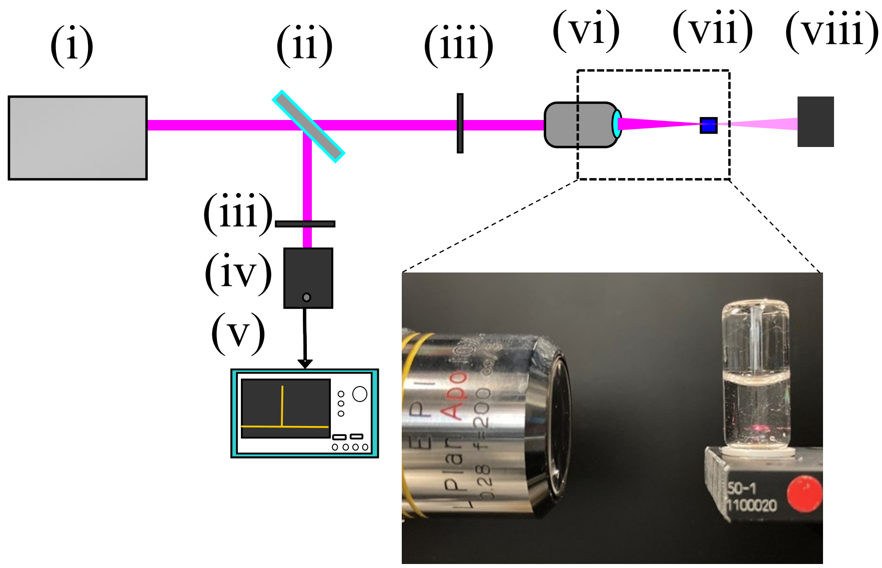


Fig. S2. Mass spectra of generated gas in **(a)** ultrapure water and **(b)** seawater.



(i) Femtosecond laser system, (ii) Half mirror, (iii) ND filter, (iv) Photo detector, (v) Digital oscilloscope, (vi) Objective lens, (vii) Cell & liquid, (viii) Power meter

Fig. S3. Experimental apparatus of the light efficiency evaluation.

References

1. Kierzkowska-Pawlaka H.; Tyczkowski J.; Jarota A.; Abramczyk H. Hydrogen Production in Liquid Water by Femtosecond Laser-Induced Plasma, *Appl. Energy* **2019**, 247, 24.
2. Mizushima Y.; Saito T. Nonlinear Bubble Nucleation and Growth Following Filament and White-Light Continuum Generation Induced by a Single-Shot Femtosecond Laser Pulse into Dielectrics Based on Consideration of the Time Scale, *Appl. Phys. Lett.* **2015**, 107, 114102.