Supplementary information

Ultrasound-assisted catalytic valorization of nitric acid waste to ammonia using hydrogen nanobubbles

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Supplementary experimental

1. Product quantification

For quantitative analysis, standard solutions of $NaNO_3$ and $NaNO_2$ with known concentrations were prepared. Calibration curves were constructed from UV–vis spectroscopy measurements using the absorbance at 303 nm for nitrate and 354 nm for nitrite (Fig. S3).

The concentrations of nitrate and nitrite in the reaction solutions before and after the reaction were determined using these calibration curves after filtration to remove catalyst and solid precipitates, and the nitrate conversion (*X*) and nitrite selectivity (*S*) were calculated using the equations below.

$$X(NO_3^-) = \frac{C(NO_3^-)_0 - C(NO_3^-)}{C(NO_3^-)_0} \times 100\%$$

$$S(NO_2) = \frac{C(NO_2)}{C(NO_3^-)_0} \times 100\%$$

For ammonia quantification, the reaction mixture was first separated into precipitate and supernatant after the reaction. The collected supernatant was then treated with 2 M sulfuric acid in an amount at least equivalent to the initial nitrate introduced into the reaction mixture. Upon acid addition, remaining Ca^{2+} ion was converted to $CaSO_4$, while the produced NH_4^+ was captured as NH_4HSO_4. The solution was then dried at 80 °C to remove water and the resulting crystalline solid was washed with acetone, weighed and analyzed by powder X-ray diffraction. Ammonia yield was calculated from the mass (*m*) of NH_4HSO_4 when $CaSO_4$ was not detected by XRD analysis. The calculated yield (*Y*) was typically 80–95% of the nitrate conversion determined by UV–vis spectroscopy, likely due to material losses during supernatant collection, the drying process, and the isolation of NH_4HSO_4 precipitates after sulfuric acid addition and acetone washing. The ammonia yield was calculated using the following equation, where *M* is the molar mass and *n* is the number of moles.

$$Y(NH_3) = \frac{m(NH_4HSO_4) \div M(NH_4HSO_4)}{n(NO_3^-)_0} \times 100\%$$

2. Wastewater treatment of nitric acid from semiconductor manufacturing process

A 6 wt% nitric acid wastewater obtained from a semiconductor manufacturing process was used for the experiment. The wastewater contained trace impurities (ppb level), including boron, sodium, aluminum, and lead. $Ca(OH)_2$ was added to obtain an approximate Ca^{2+}/NO_3^- ratio of 0.5, after which the mixture was filtered to remove insoluble solid prior to the reaction. The subsequent procedure followed the general reaction procedure.

3. Preliminary comparison of electrical power consumption

A preliminary laboratory-scale comparison of electrical power consumption was conducted between a mechanically stirred reactor and the present ultrasonic reactor under identical reaction conditions. The experiments were performed until nitrate conversions exceeded 90%. Electrical power consumption was monitored using a plug-in power meter connected to each reactor system. Under these conditions, the ultrasonic reactor exhibited significantly lower electrical power consumption compared to the specific mechanically stirred system used in this study.

Supplementary tables

Table S1 Reaction conditions for additional experiments.

Entry [a]	$[NO_3^-]$ (M)	Total volume (mL)	Ca^{2+}/NO_3^- mole ratio	Temperature (°C)	NO_3^- conversion (%)	NO_2^- selectivity (%)
1	1	50	0	100	4.6	HNO_2
2	1	50	0.38	100	4.8	HNO_2
3[b]	1	50	0.5	100	13.2	n.d.
4	1	50	0.62	100	6.2	n.d.
5[c]	1	50	0.5	100	14.3	0.50
6[d]	0.2	50	0.5	100	98.3	-
7	0.2	100	0.5	100	98.1	-
8[e]	0.2	50	0.5	100	99.7	-
9[c]	0.2	50	0.5	60	99.9	-
10[c]	0.5	4	0.5	60	94.7	-

[a] All reactions were conducted using 0.1 g of H_xRuO_2 under 10 bar of H_2 at 2.4 MHz and 11.84 W for 4 hours unless otherwise stated. [b] Entry 6 of Table 1. [c] Experiments were conducted in a conventional pressure reactor with stirring at 300 rpm. [d] $Ca(NO_3)_2{\cdot}4H_2O$ (10 mmol) was used in place of $Ca(OH)_2$ and nitric acid. [e] Experiment was performed using filtered nitric acid leachate derived from semiconductor manufacturing processes including boron, sodium, aluminum, and lead.

Table S2 Comparison of energy requirements of conventional catalytic reactor and ultrasonic reactor.[a]

Reactor setup	Parr 4560 reactor with a Parr 4848 controller and an external chiller [b]	Hotplate stirrer with an oil bath without condenser [c]	Custom-built ultrasonic reactor with a cooling fan [d]
Power consumption (W)	522	54	131
Efficiency (kWh/mol)[h]	209[e]	228[f]	53[g]

[a] Power consumption was measured using plug-in power meter. [b] Experimental setup as in Fig. S6a (60 °C, 300 rpm). [c] Experimental setup as in Fig. S6b (60 °C, 300 rpm). [d] Experimental setup as in Fig. S2 (60 °C, 2.4 MHz and 11.84 W). [e] Entry 8 in Table S1. [f] Enry 9 in Table S1. [g] Entry 7 in Table 1. [h] Calculated assuming 100% ammonia selectivity.

Supplementary figures

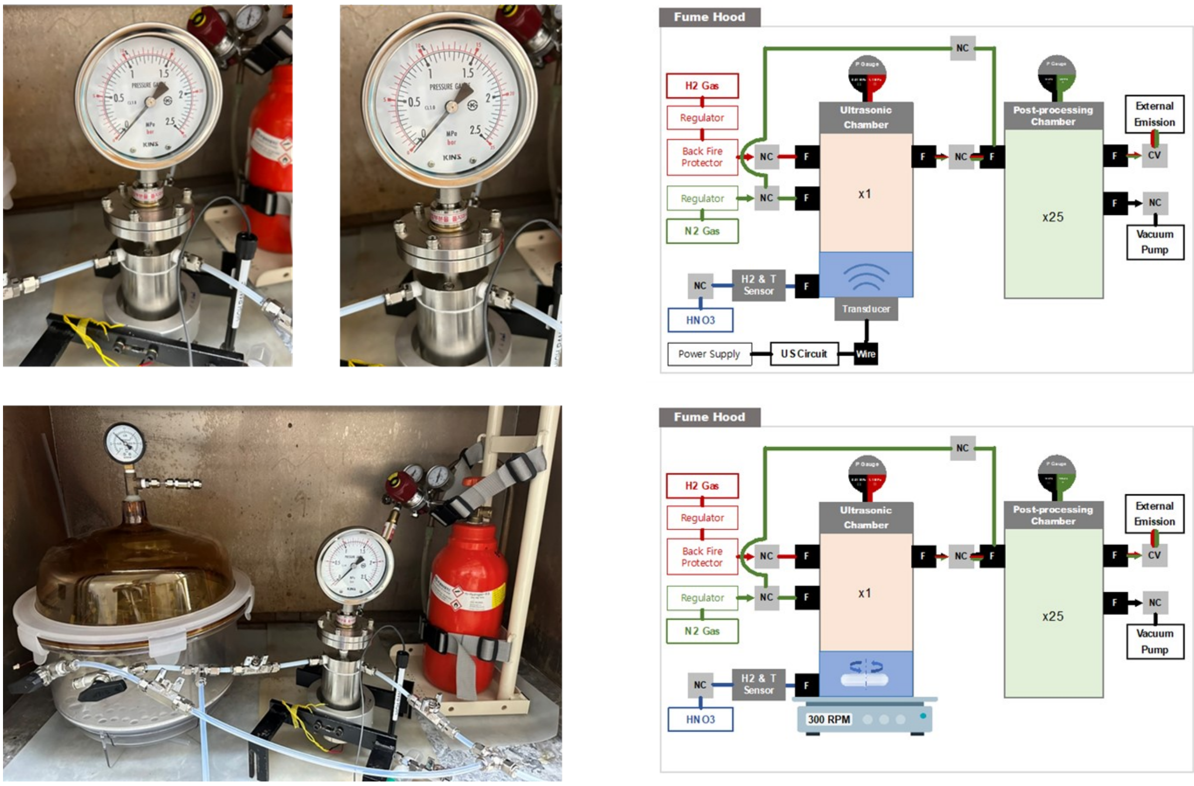

Fig. S1 Custom-built, atomization-assisted ultrasonic apparatus for H_2 nanobubble generation and stability measurements.

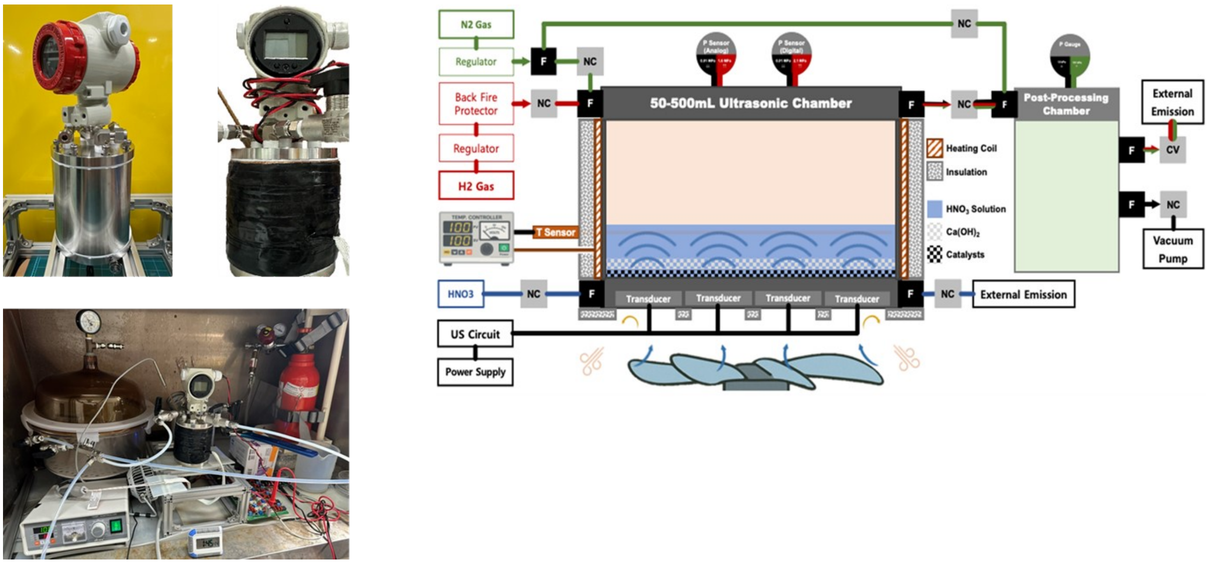

Fig. S2 Experimental setup for ultrasound-assisted catalytic nitrate-to-ammonia conversion using a custom-built cylindrical reactor.

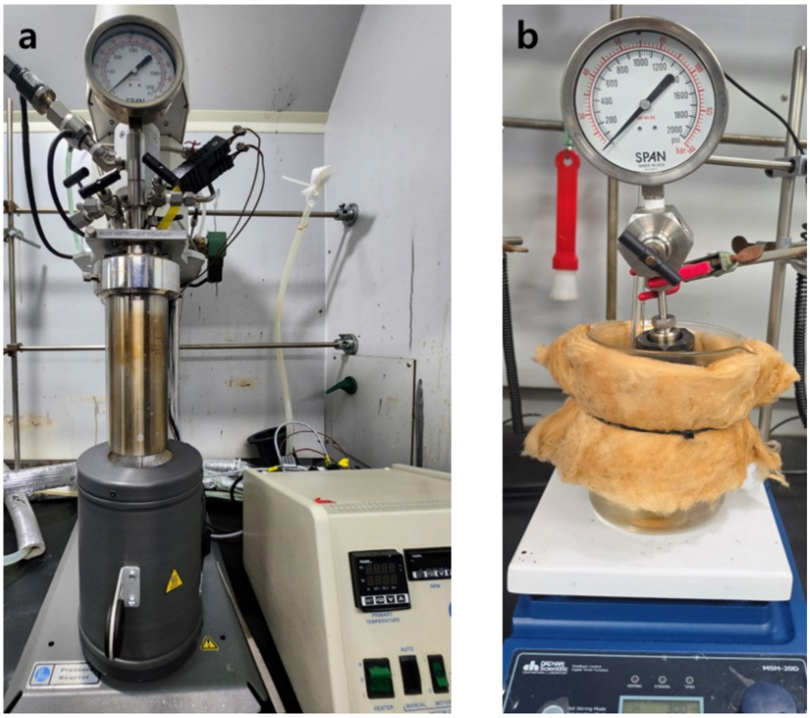

Fig. S3 Experimental setup for nitrate-to-ammonia conversion using a conventional catalytic reactor for control experiment. (a) Parr 4560 reactor (600 mL) with a Parr 4848 controller and an external chiller. (b) Hotplate stirrer with an oil bath without condenser.

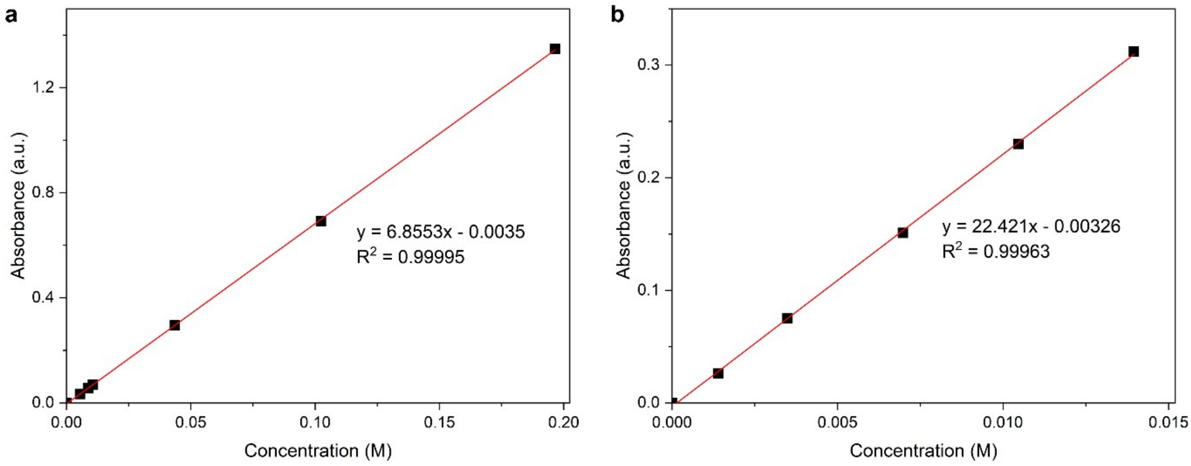

Fig. S4 Calibration curves for nitrate and nitrite quantification obtained by UV−vis spectroscopy at (a) 303 nm for nitrate and (b) 354 nm for nitrite.

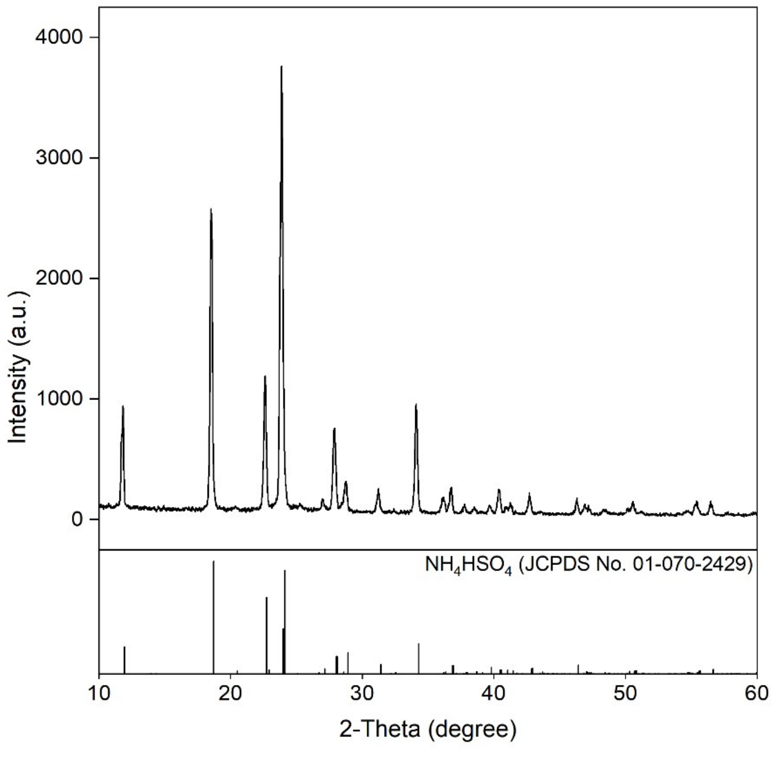

Fig. S5 XRD pattern of the ammonium bisulfate (NH_4HSO_4) precipitate. The pattern of the product, precipitated as ammonium bisulfate, confirms it as the sole crystalline phase when nitrate hydrogenation completed.

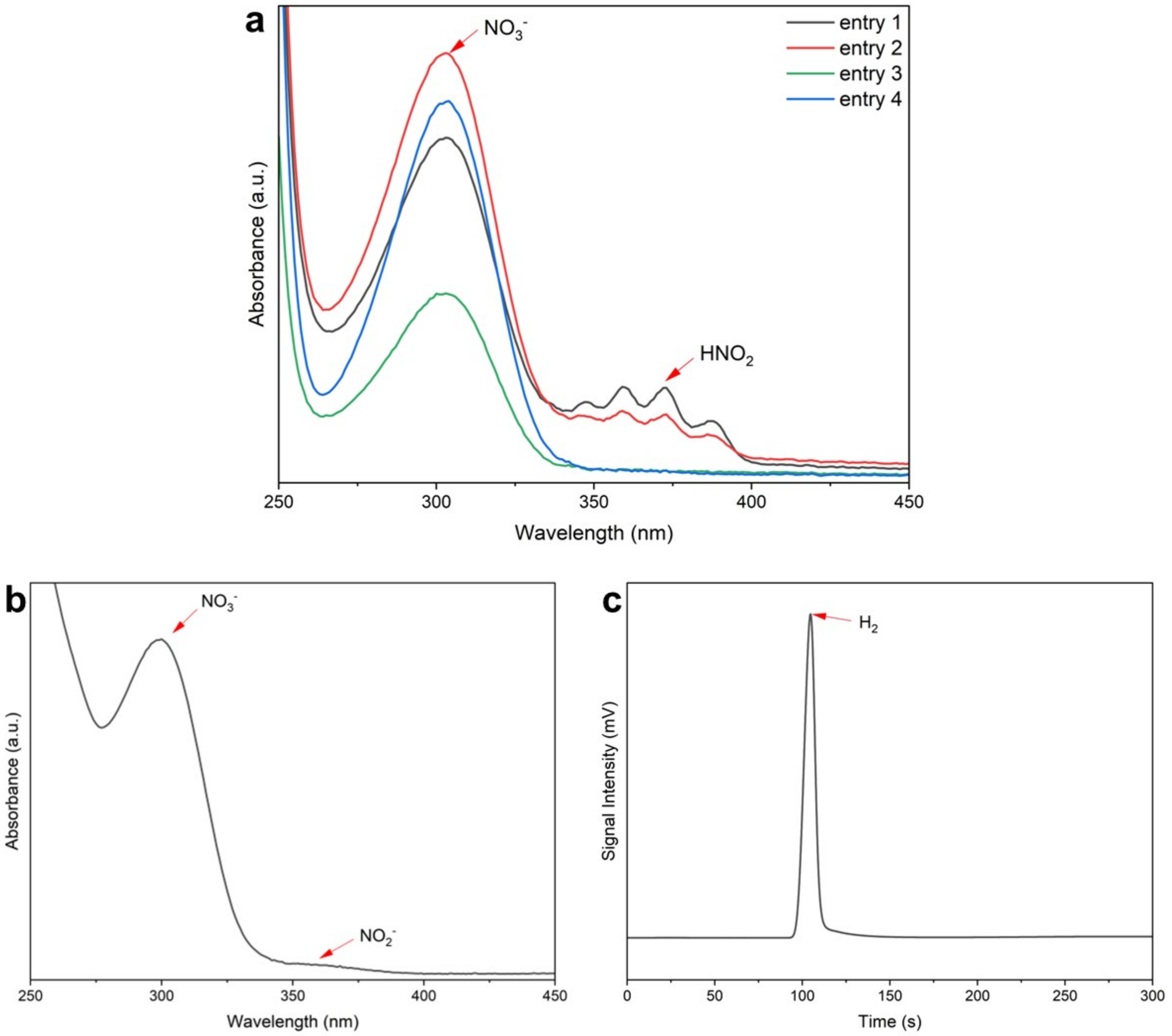

Fig. S6 (a) UV−vis absorption spectrum of the solution after the reaction corresponding to Entry 1−4 in Table S1. The spectrum shows a characteristic absorption peak of the nitrous acid (HNO_2) intermediate, indicating that ammonia selectivity decreases under $Ca(OH)_2$ deficient conditions compared with Ca^{2+}/NO_3^- = 0.5 condition. Under these conditions (Entry 1, 2 in Table S1), the medium remains relatively acidic, and nitrite is therefore likely present in equilibrium with nitrous acid (HNO_2). (b) UV−vis absorption spectrum and (c) gas chromatography data for Entry 5 in Table S1. Nitrite selectivity was 0.50%, and no gaseous products, such as N_2, N_2O, or NO_2, were detected apart from the reactant H_2.