Experimental Section

Preparation of SnO_2 nanofibers: $SnCl_4•5H_2O$ (1.2 g) was added to *N,N*-dimethylformamide (7.6 g), and stirred continuously until it was completely dissolved. Next, poly(vinyl pyrrolidone) (1.2 g) was added to the above solution, and stirred for 12 h to obtain a clear and transparent solution. It was then subjected to electrospinning by using a DXES-13 spinning equipment at an electrostatic voltage of 20 kV, a propulsion velocity of 2.0 mL h^{-1}, a receive distance of 10 cm, and a relative humidity of 20±5%. The as-spun hybrid nanofibers were then heated at a heating rate of 2 °C min^{-1} to 600 °C, and kept for 2 h to remove the organic component and obtain neat SnO_2 nanofibers.

Preparation of Sb_2S_3@SnO_2 nanofibers: Antimony(III) acetate (0.3 g) was added to deionized water (30 mL) and stirred for 20 min, to which thiourea (0.3 g) was added and stirred for another 20 min. The as-prepared SnO_2 nanofibrous membrane (0.05 g) was immersed in the above solution, which was transferred to a Teflon-lined stainless-steel autoclave (50 mL). The autoclave was kept at 150 °C for 8 h, and cooled naturally to room temperature. The product was taken out, washed by absolute ethanol and deionized water, and dried at 80 °C for 12 h.

Electrocatalytic NRR tests: An electrocatalyst ink was prepared by adding the Sb_2S_3@SnO_2 nanofibers (1 mg) to 5 wt% Nafion solution (20 μL) and ethanol (80 μL). The electrocatalyst ink was sonicated for 1 h, pipetted onto a nickel foam (1×1 cm^2), and vacuum-dried as the working electrode. Note that the nickel foam was pre-treated by soaking in acetone and 1 M HCl to remove the organic impurities and the oxide layer, separately. The counter electrode was a platinum mesh, and the reference electrode was a saturated calomel electrode (SCE). The NRR experiments were conducted in a two-compartment electrocatalysis cell under ambient conditions, and the separator was a Nafion 211 membrane. The compartments were filled with 0.1 M Na_2SO_4, and bubbled with high-purity nitrogen (99.999%) for at least

30 min before experiments. The potentials were converted to the reversible hydrogen electrode (RHE) based on the following equation:

$$E\ (vs.\ \mathrm{RHE}) = E\ (vs.\ \mathrm{Hg/HgO}) + 0.059 \times \mathrm{pH} + 0.242\ \mathrm{V} \qquad (1)$$

The ammonia yield and faradaic efficiency were determined according to our previous report (*Angew. Chem. Int. Ed.*, 2019, DOI: 10.1002/anie.201908415). For the isotopic labelling, the cathodic compartment was bubbled with Ar for at least 30 min, and then bubbled with $^{15}N_2$ (99 at%) or $^{14}N_2$ for electrolysis at –0.4 V *vs.* RHE for 24 h. The products were collected by distillation, dissolved in dimethyl sulfoxide-D6, and subjected to ^1H NMR spectroscopy.

Characterizations: SEM was performed by a Tescan VEGA3 microscope operated at an accelerating voltage of 20 kV. TEM was performed by a JEOL JEM-2010 microscope operated at an accelerating voltage of 120 kV. XRD was performed by a Bruker D8 Advanced X-ray diffractometer with Cu Kα radiation ($\lambda = 0.154$ nm). XPS was performed by an Escalab 250Xi spectrometer. ^1H NMR was performed by a Bruker AVANCE III HD spectrometer (600 MHz). UV-vis was performed by a Hitachi U-3900 spectrophotometer. The chronoamperometry curves were recorded by a Bio-Logic VSP electrochemical workstation.

Supplementary Figures

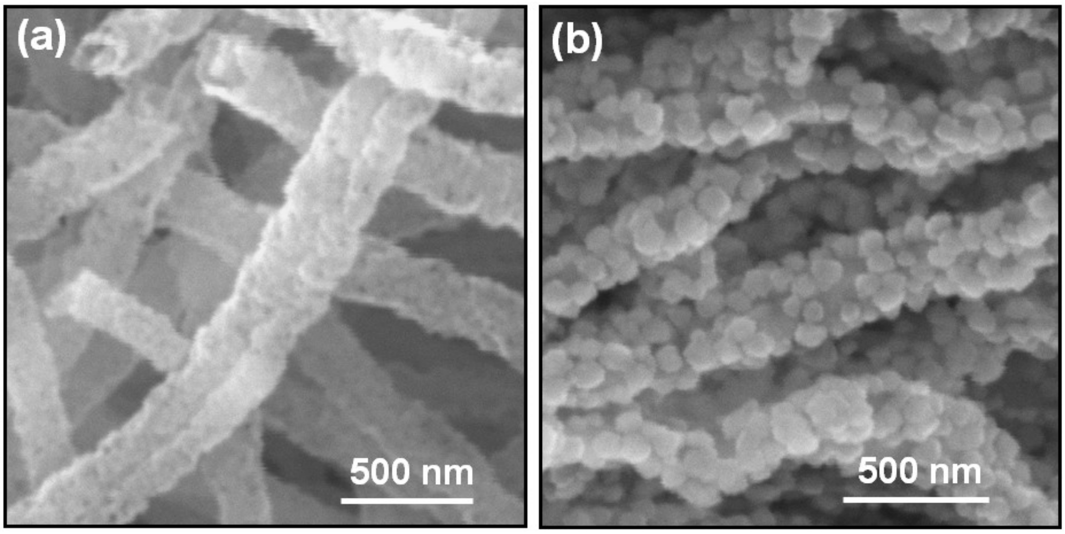

Figure S1. SEM images (a) SnO_2 nanofibers and (b) $Sb_2S_3@SnO_2$ nanofibers.

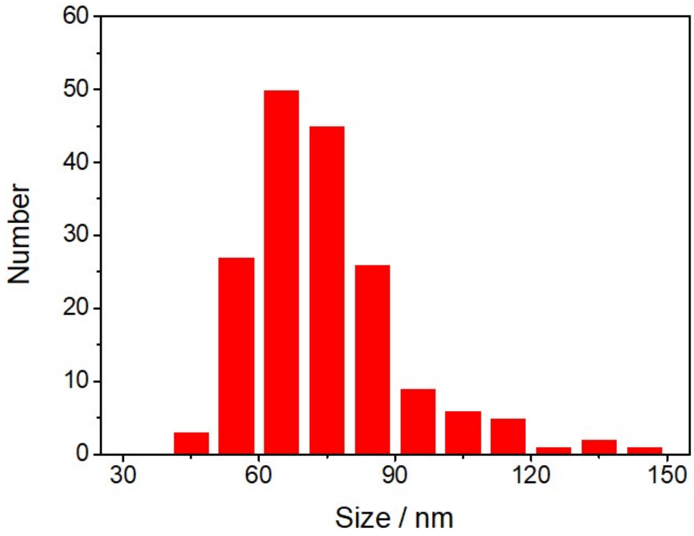

Figure S2. Statistics on the Sb_2S_3 nanoparticle sizes.

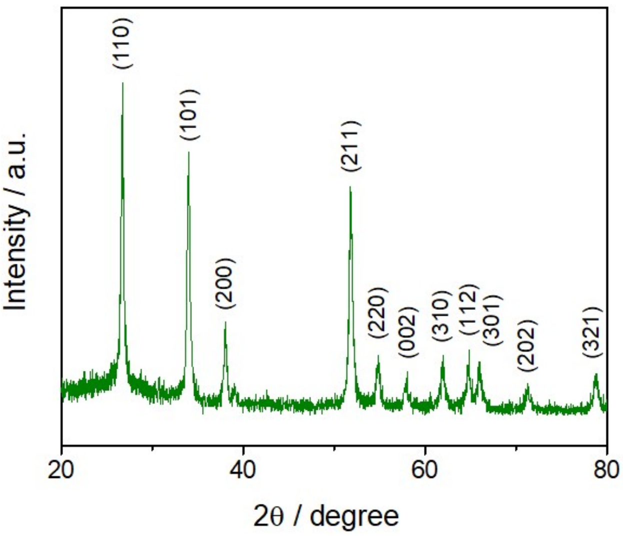

Figure S3. XRD pattern of neat SnO_2 nanofibers.

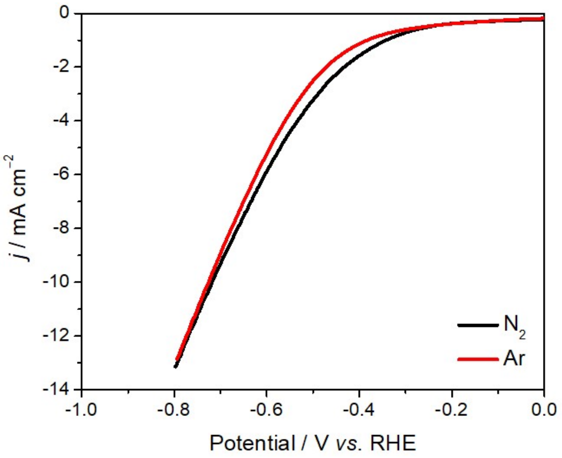

Figure S4. LSV curves of Sb_2S_3@SnO_2 nanofibers electrolyzed in N_2- and Ar-saturated 0.1 M Na_2SO_4.

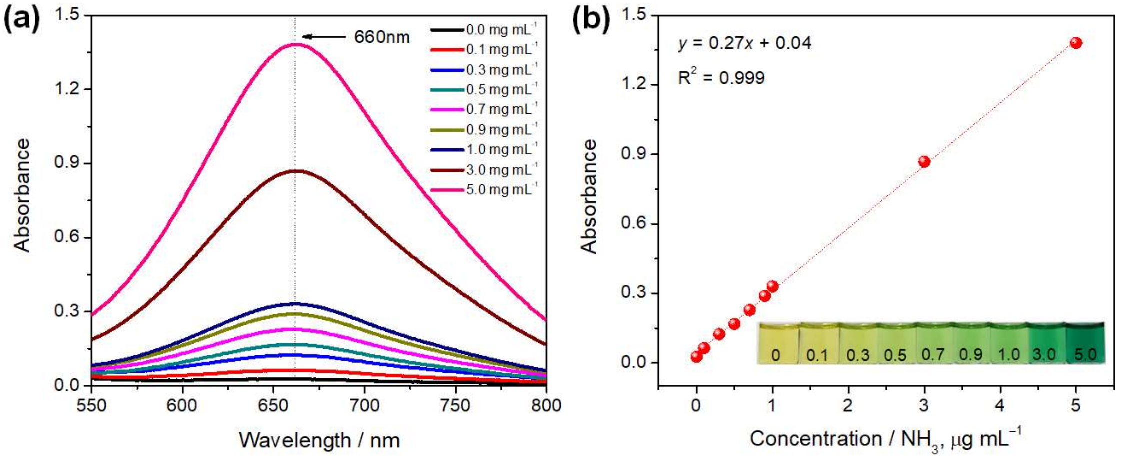

Figure S5. (a) UV-vis absorption spectra at various ammonia concentrations after being incubated for 2 h at room temperature, and (b) the corresponding calibration curve.

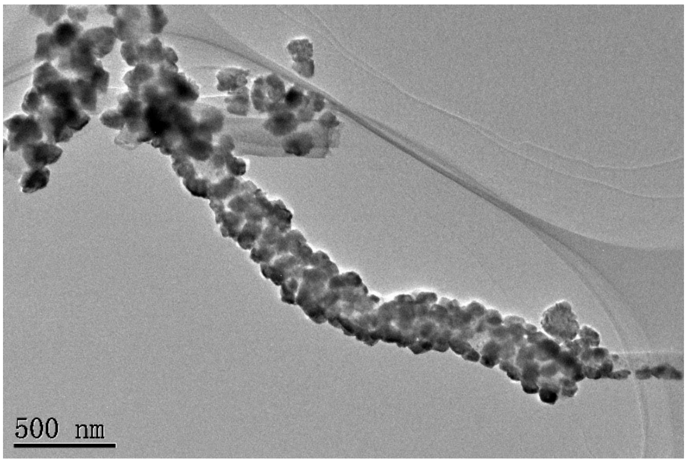

Figure S6. TEM image of Sb_2S_3@SnO_2 nanofibers after electrolysis at –0.4 V *vs.* RHE for 24 h.

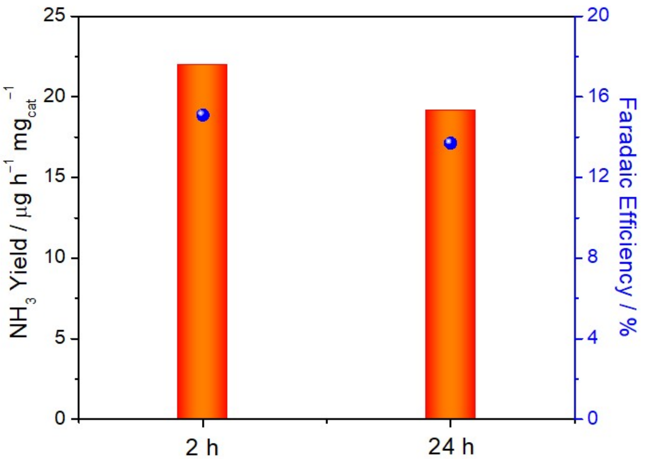

Figure S7. Ammonia yields and faradaic efficiencies of Sb_2S_3@SnO_2 nanofibers after electrolysis at –0.4 V *vs.* RHE for 2 and 24 h, respectively.

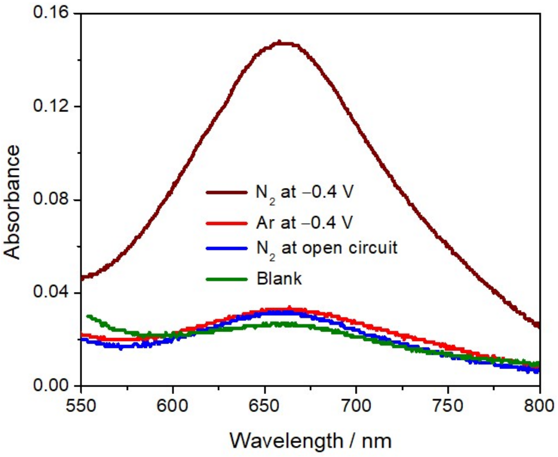

Figure S8. UV-vis absorption spectra of the electrolytes (stained by Nessler's reagent) after 2 h electrolysis in argon at –0.4 V *vs.* RHE, and in nitrogen under open circuit.

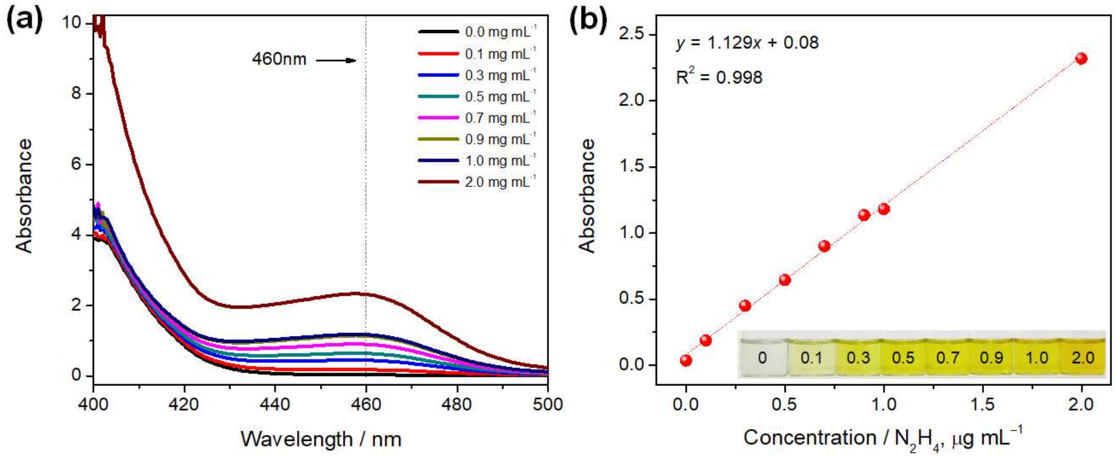

Figure S9. (a) UV-vis absorption spectra at various hydrazine concentrations after being incubated for 2 h at room temperature, and (b) the corresponding calibration curve.

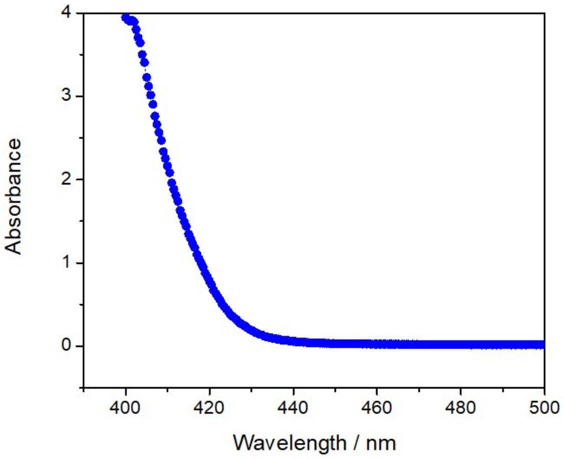

Figure S10. UV-vis absorption spectrum of the electrolyte after electrolysis at –0.4 V *vs.* RHE for 2 h.

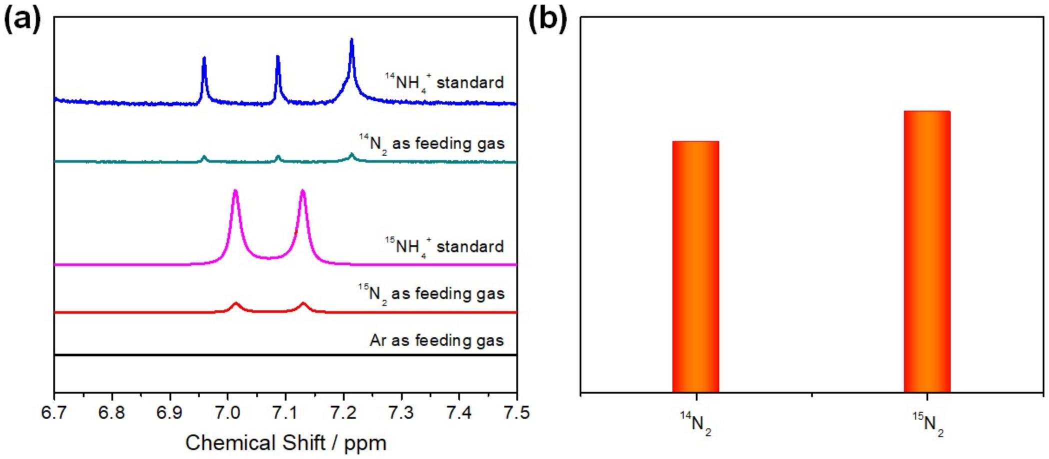

Figure S11. (a) ^1H NMR spectra and (b) integral areas of $^{15}N_2$ and $^{14}N_2$-saturated electrolytes after electrolysis at –0.4 V *vs.* RHE for 24 h.