Electronic Supplementary Information

Determination of NH_3

The indophenol blue method was used to determine the measurement of ammonia production by NRR. The electrolyte was collected after chronopotentiometric measurements for 2 h, and then 2 mL of chromogenic reagent (1 M NaOH, 5 wt% $C_7H_6O_3$, 5 wt% $C_6H_5Na_3O_7$), 1 mL of oxidizing solution (0.05 M NaClO) and 0.2 mL of catalysing reagent (1 wt% $Na_2[Fe(CN)_5NO]$) were sequentially added to the 2 mL of the electrolyte. The mixed solution after being left in the dark for 2 h was measured using the ultraviolet−visible (UV−vis) spectrophotometer by a TU-1900 spectrophotometer. A series of standard ammonium chloride (NH_4Cl) solutions were used to calibrate the concentration–absorbance curve. The ammonia yield (r_{NH3}) and Faradaic efficiency (FE) was calculated using the following equation:

$$r_{NH_3} = (c_{NH_3} \times V)/t \times m \quad (1)$$

$$FE = (3F \times c_{NH_3} \times V)/(17 \times Q) \quad (2)$$

Where c_{NH3} (μg mL^{-1}) is the measured NH_3 concentration, V (mL) is the electrolyte volume, t (h) is the electrolysis time, m (mg) is the catalyst mass, F (96 485 C mol^{-1}) is the Faraday constant, and Q (C) is the total charge during electrolysis.

Determination of N_2H_4

The method of Watt and Chrisp were used to determine the byproduct of hydrazine. *p*-dimethylaminobenzaldehyde (5.99 g) dissolved in a mixed solution of hydrochloric acid (30 mL) and absolute ethanol (300 mL) was used as the chromogenic reagent, and the above chromogenic reagent (5 mL) was added to the electrolytic solution (5 mL) after electrolysis. Then, the mixed solution for 20 min was measured using the UV−vis absorption spectrum. The concentration-absorbance curves for standard solution of hydrazine at different concentrations was used to calculate the byproduct of hydrazine yield.

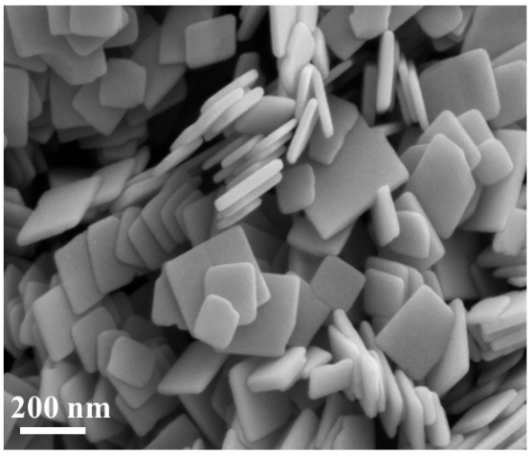

Fig. S1 SEM image of the BiOCl NPs.

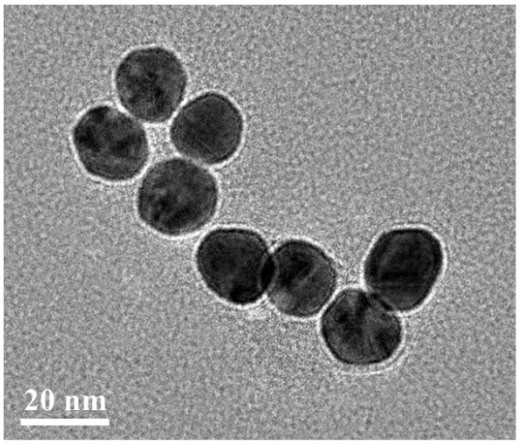

Fig. S2 TEM image of the Au nanoparticles.

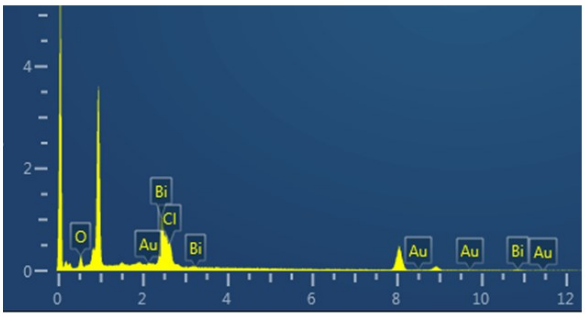

Fig. S3 EDX spectrum of the Au/BiOCl NPs.

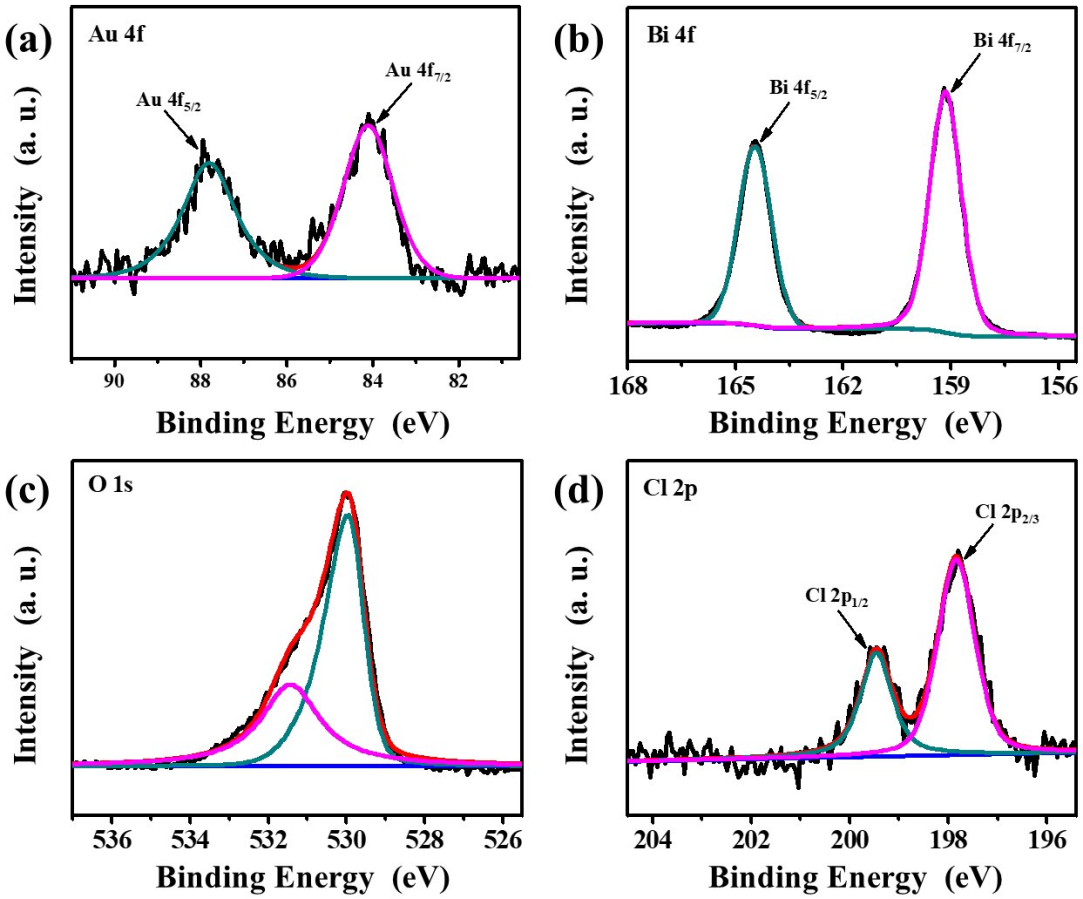

Fig. S4 (a) Au 4f, (b) Bi 4f, (c) O 1s and (d) Cl 2p high-resolution XPS spectra of the Au/BiOCl NPs.

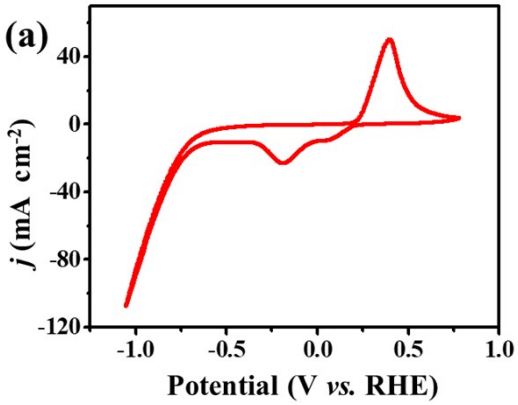

Fig. S5 CV curve of the Au/BiOCl NPs in 0.1 M HCl electrolyte with a scan rate of 100 mV s^{-1}.

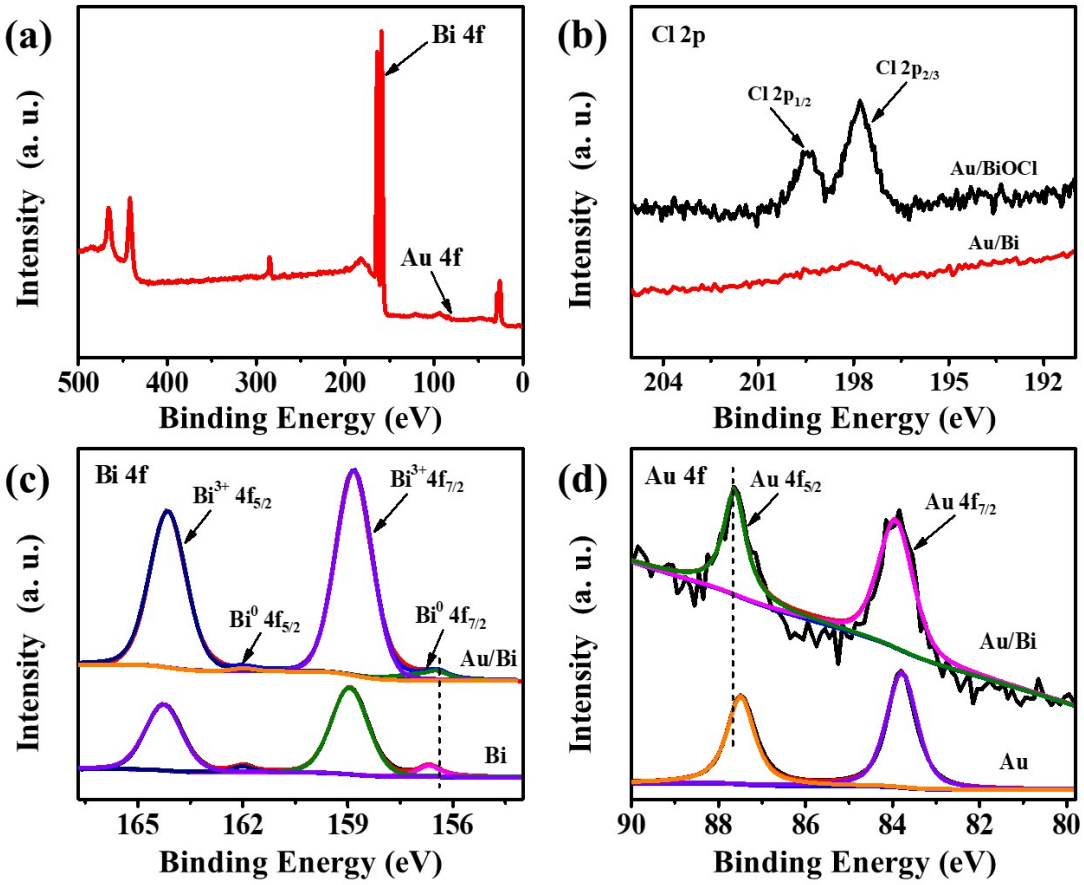

Fig. S6 (a) XPS survey spectrum of the Au/Bi NSs. (b) Cl 2p XPS spectra of the Au/BiOCl NPs and Au/Bi NSs. (c) Bi 4f XPS spectra of the Au/Bi NSs and Bi NSs. (c) Au 4f XPS spectra of the Au/Bi NSs and Au NPs.

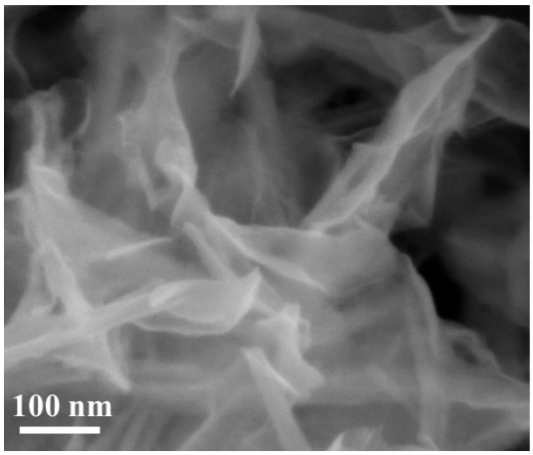

Fig. S7 SEM image of the Bi NSs.

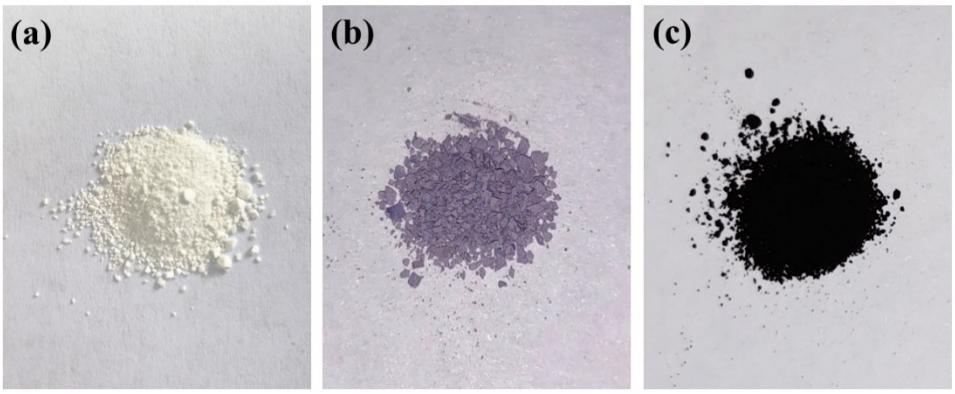

Fig. S8 The sample photo of (a) BiOCl NPs, (b) Au/BiOCl NPs and (c) Au/Bi NSs.

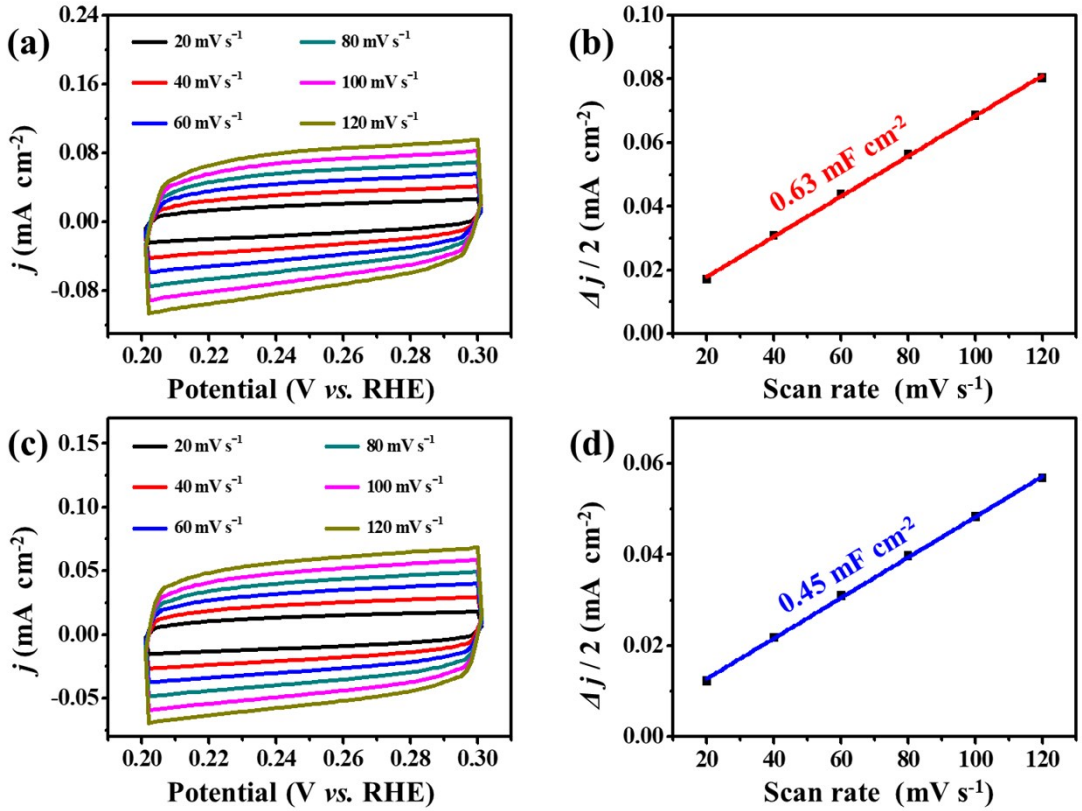

Fig. S9 (a, c) CV curves obtained with different scan rates in 0.1 M HCl aqueous solution and (b, d) capacitive current densities at 0.25 V (*vs.* RHE) for various catalysts: (a, b) Au/Bi NSs, (c, d) Au/BiOCl NPs.

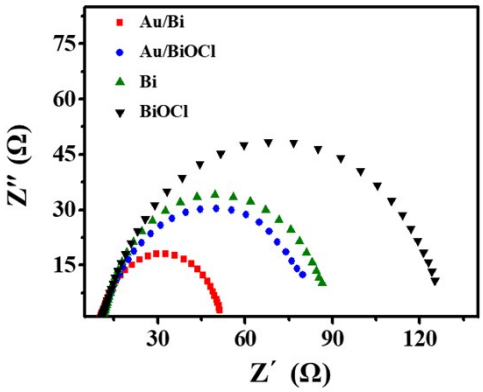

Fig. S10 EIS spectra of different samples at -0.62 V (*vs.* RHE) in a frequency range from 1 Hz to 100 kHz.

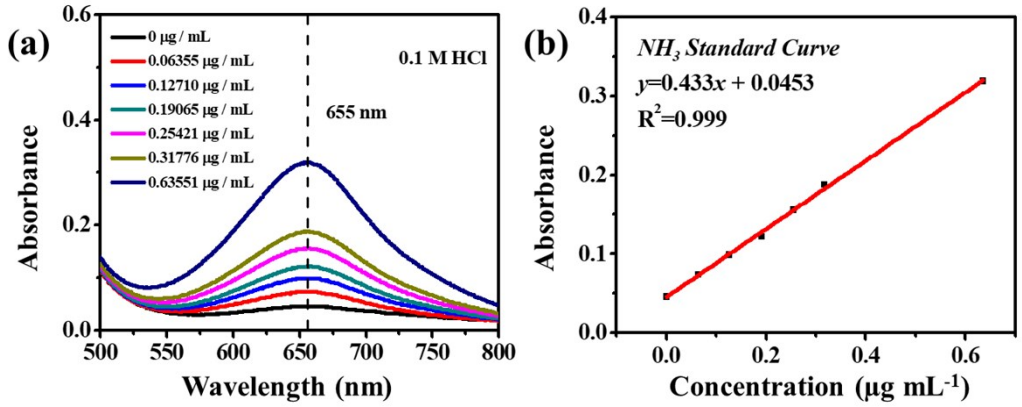

Fig. S11 (a) UV-vis absorption spectra of indophenol assays with various NH_4^+ ions concentrations after incubated for 2 h at room temperature. (b) the concentration–absorbance curve used to estimate the concentrations of NH_3.

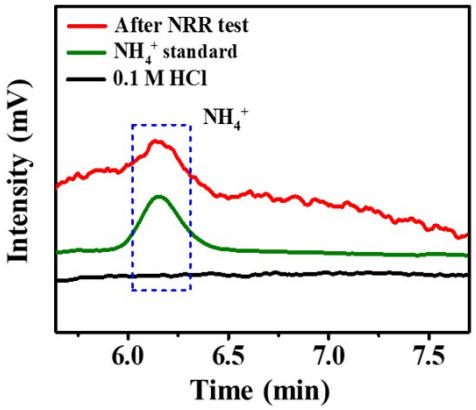

Fig. S12 Ion chromatography of the electrolyte using Au/Bi NSs for NRR at -0.3 V (vs. RHE).

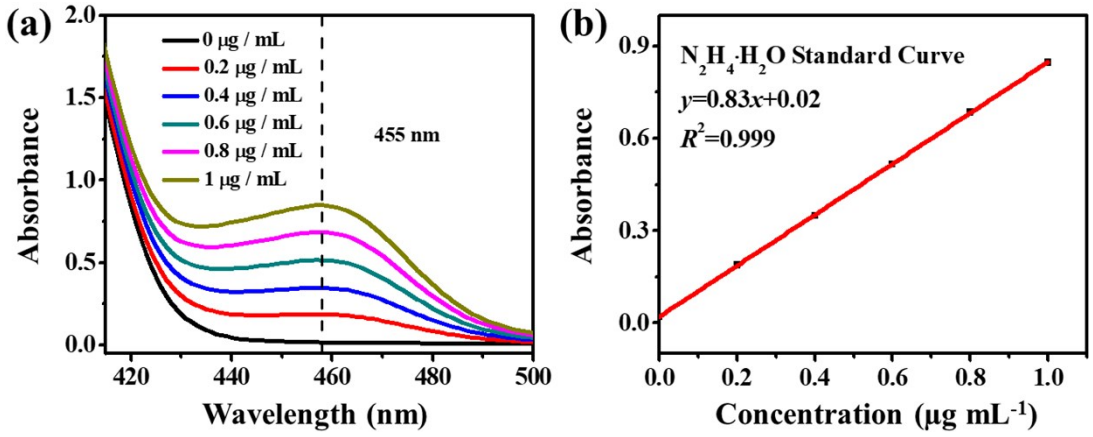

Fig. S13 (a) UV-vis absorption spectra of various $N_2H_4 \cdot H_2O$ concentrations after incubated for 20 min at room temperature. (b) The calibration curve used for estimation of N_2H_4 concentration.

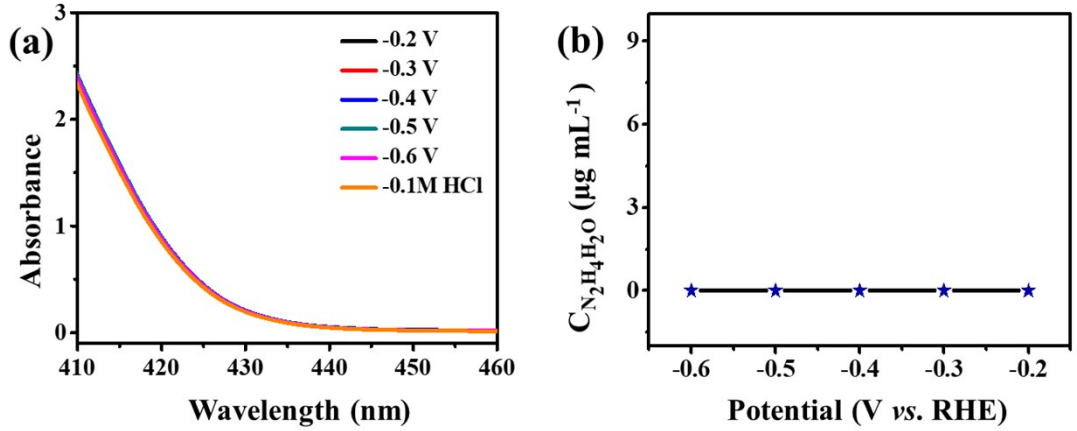

Fig. S14 (a) UV−vis absorption spectra and (b) the $N_2H_4 \cdot H_2O$ concentration of the electrolyte with the indicator for 20 min after electrolysis using Au/Bi NSs at different potentials for 2 h.

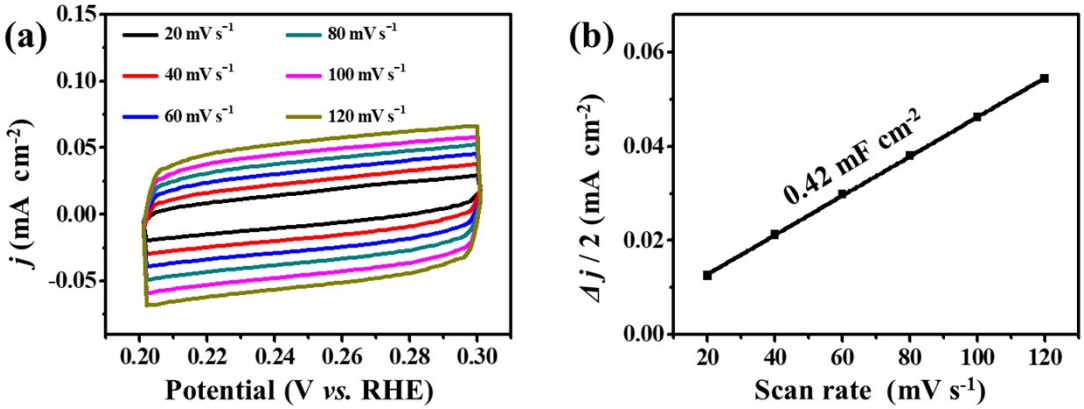

Fig. S15 (a) CV curves obtained with different scan rates in 0.1 M HCl aqueous solution and (b) capacitive current densities at 0.25 V (*vs.* RHE) for the Bi NSs.

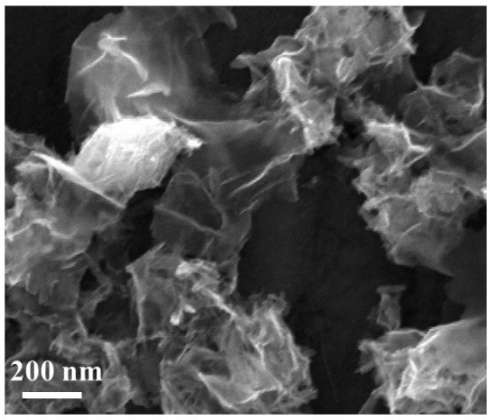

Fig. S16 SEM image of the Au/Bi NSs after electrocatalytic stability testing.

Table S1. Performance comparison between the as-prepared Au/Bi NSs and some other reported electrocatalysts in HCl solutions.

Electrocatalysts	**Electrolytes**	**NH_3 yield rate**	**FE(%)**	**Ref.**
Au/Bi NSs	**0.1 M HCl**	**20.39 μg h^{-1} $mg^{-1}_{cat.}$ (8.16 μg h^{-1} cm^{-2})**	**15.53**	**This work**
Bi NS/CF	0.1 M HCl	5.26 μg h^{-1} $mg^{-1}_{cat.}$	10.26	[1]
PCN-NV4	0.1 M HCl	8.09 μg h^{-1} $mg^{-1}_{cat.}$	11.59	[2]
a-Au/CeO_x-RGO	0.1 M HCl	8.3 μg h^{-1} $mg^{-1}_{cat.}$	10.10	[3]
$LiMn_2O_4$ NF/CP	0.1 M HCl	15.83 μg h^{-1} $mg^{-1}_{cat.}$	7.44	[4]
Ta_2O_5 nanorods	0.1 M HCl	15.9 μg h^{-1} $mg^{-1}_{cat.}$	8.9	[5]
TiO_2	0.1 M HCl	3.0 μg h^{-1} $mg^{-1}_{cat.}$	6.5	[6]
N-doped carbon	0.1 M HCl	15.7 μg h^{-1} $mg^{-1}_{cat.}$	1.45	[7]
O-CN/CP	0.1 M HCl	20.15 μg h^{-1} $mg^{-1}_{cat.}$	4.97	[8]
Ti_3C_2Tx nanosheet	0.1 M HCl	20.4 μg h^{-1} $mg^{-1}_{cat.}$	9.3	[9]
VN/TM	0.1 M HCl	3.57 μg h^{-1} $mg^{-1}_{cat.}$	2.25	[10]
Ag nanosheet	0.1 M HCl	2.83 μg h^{-1} cm^{-2}	4.8	[11]

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