Electronic Supplementary Material (ESI) for ChemComm.
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Experimental Section

A flexible TiO_2 nanofibrous membrane was fabricated according to our previous report (*Angew. Chem. Int. Ed.*, 2019, **58**, 18903). Next, sodium tungstate (0.49 g), thiourea (0.56 g), acetic acid (250 μL) and deionized water (25 mL) were mixed under continuous stirring at room temperature for 4 h, and transferred to a Teflon-lined stainless-steel autoclave. The flexible TiO_2 nanofibrous membrane was immersed in this mixed solution, kept at 180 °C for 9 h, cooled naturally, washed with deionized water and absolute alcohol, and dried to obtain needle-constructed WO_3 nanoflowers fixed on the TiO_2 nanofibers. For P doing, triethyl phosphate (50 μL) was added to the mixed solution, and all the following procedures were the same.

SEM was performed by Tescan VEGA3 microscope at 20 kV accelerating voltage. TEM was performed by JEOL JEM-2010 microscope at 120 kV accelerating voltage. XRD was performed by Bruker D8 Advance X-ray diffractometer with Cu Kα radiation (λ = 0.154 nm). XPS was performed by ULVAC-PHI Quantera SXM spectrometer. Raman was performed by Renisaw inVia Reflex spectrometer (λ = 532nm). ^{1}H NMR was performed by a Bruker Avance III HD spectrometer. UV-vis was performed by Hitachi U-3900 spectrophotometer.

The electrocatalytic NRR experiments were conducted in an H-type electrolysis cell, with a piece of WO_3@TiO_2 or P-WO_3@TiO_2 nanofibrous membrane (effective area: 0.5×0.5 cm^2) used as the cathode, a platinum mesh used as the anode, a saturated

calomel electrode (SCE) used as the reference electrode. The two cells were filled with 120 mL of 0.1 M Na_2SO_4, and separated by a Nafion 212 membrane. The chronoamperometry curves were recorded by a Bio-Logic VSP electrochemical workstation. The NH_3 and N_2H_4 yields were determined by the indophenol blue method and the Watt and Chrisp method, respectively. The details could be found in our previous report (*Angew. Chem. Int. Ed.*, 2019, **58**, 18903).

The isotopic labelling experiment was conducted through electrolysis in the atmosphere of $^{15}N_2$ (Wuhan Newradar Special Gas Co., Ltd.) at –0.55 V *vs.* RHE for 12 h. The electrolyte was then collected, concentrated by distillation, and dissolved in dimethyl sulfoxide-D6 for ^{1}H NMR characterization. As a control, the standard $^{15}NH_4^+$ sample was also dissolved in dimethyl sulfoxide-D6 for ^{1}H NMR characterization.

Supplementary Figures

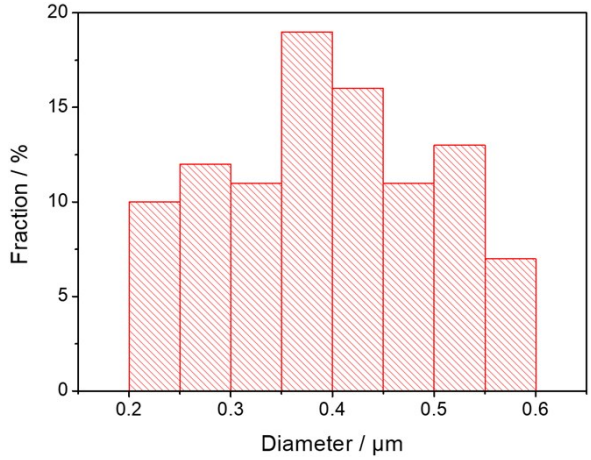

Figure S1. Statistics on the diameters of TiO_2 nanofibers.

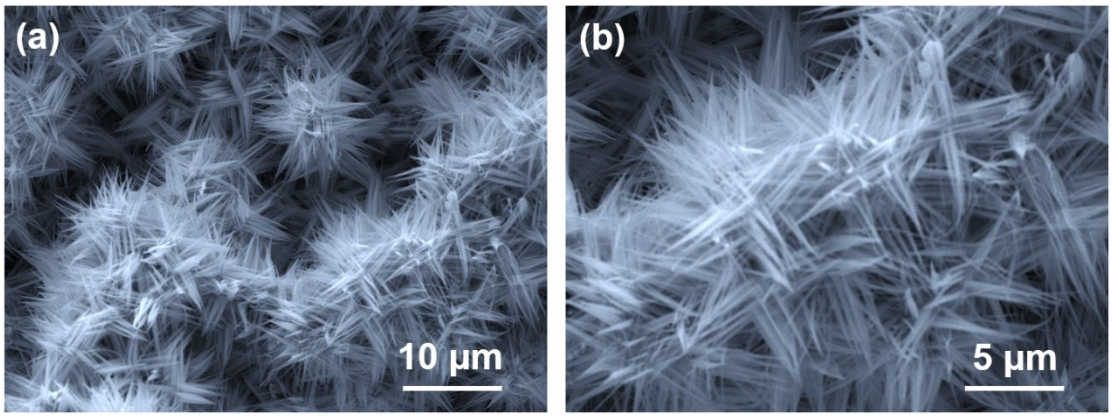

Figure S2. (a) Low- and (b) high-magnification SEM images of nanoneedle-constructed WO_3 flowers fixed on TiO_2 nanofibrous membrane.

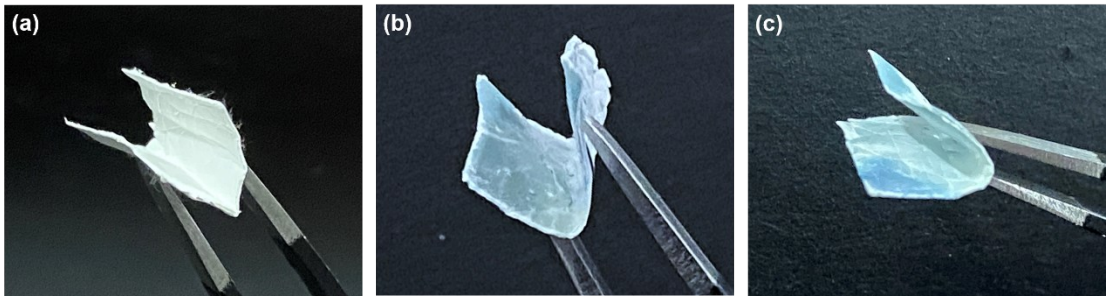

Figure S3. Digital images of (a) TiO_2, (b) WO_3@TiO_2 and (c) P-WO_3@TiO_2 nanofibrous membranes showing their excellent robustness and flexibility.

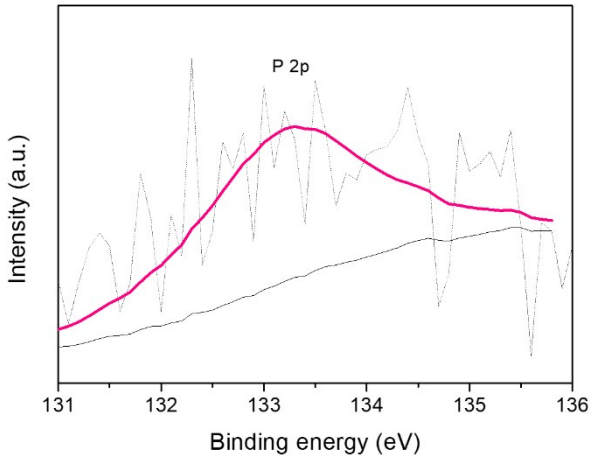

Figure S4. High-resolution P 2p XPS spectrum of P-WO_3@TiO_2 nanofibrous membrane.

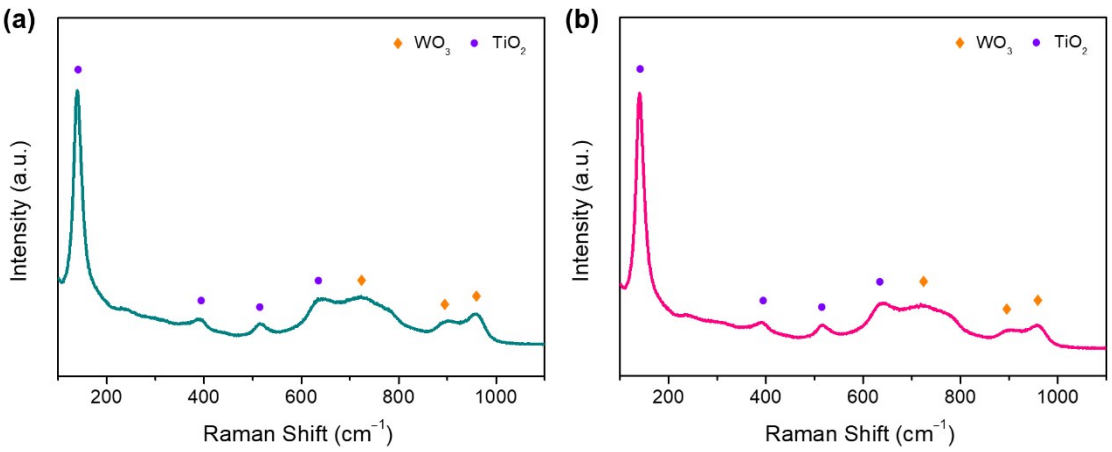

Figure S5. Raman spectra of WO_3@TiO_2 and P-WO_3@TiO_2 nanofibrous membranes.

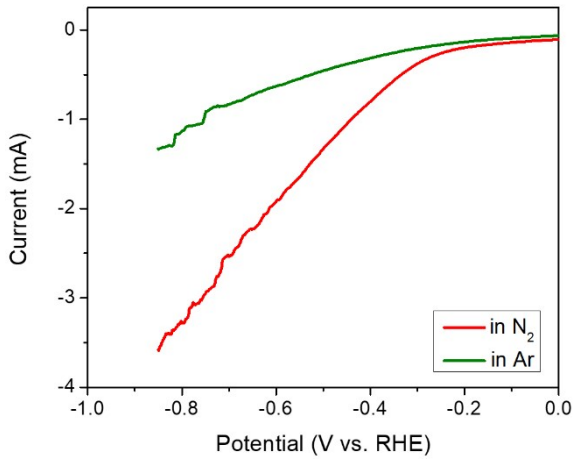

Figure S6. LSV curves of P-WO_3@TiO_2 nanofibrous membrane in N_2- and Ar-saturated electrolytes.

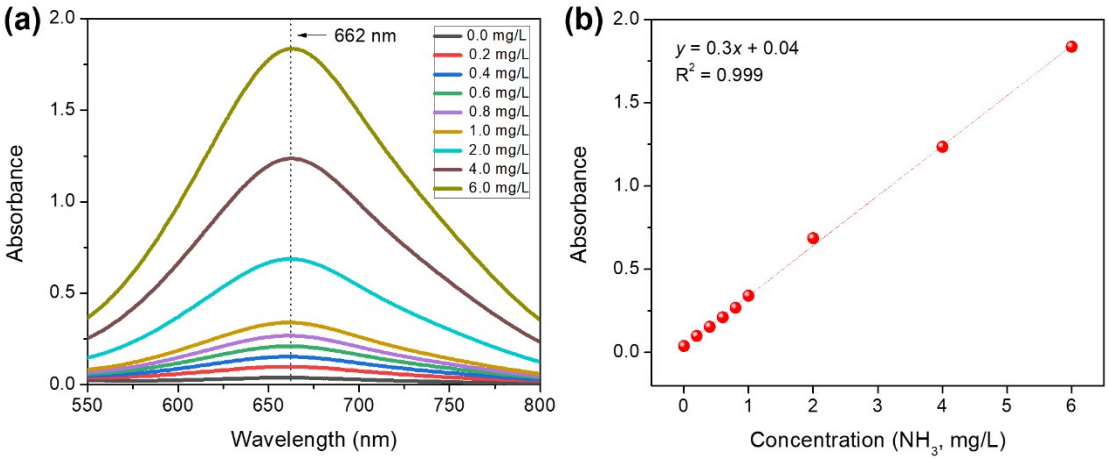

Figure S7. (a) UV-vis spectra and (b) calibration curve of NH_3 solutions with different concentrations based on the indophenol blue method.

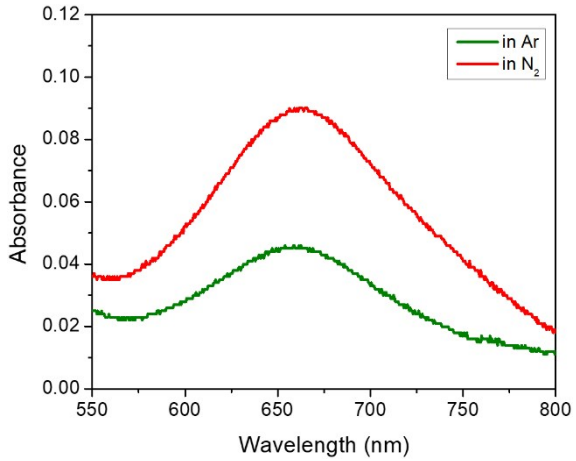

Figure S8. UV-vis spectra of the electrolytes after 2 h electrolysis in N_2 and Ar at –0.55 V *vs.* RHE (in the presence of P-WO_3@TiO_2 nanofibrous membrane).

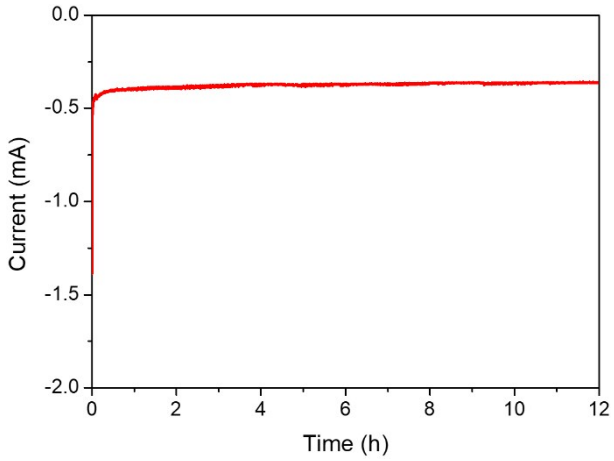

Figure S9. Long-term chronoamperometry curve of P-WO_3@TiO_2 nanofibrous membrane at –0.55 V *vs.* RHE.

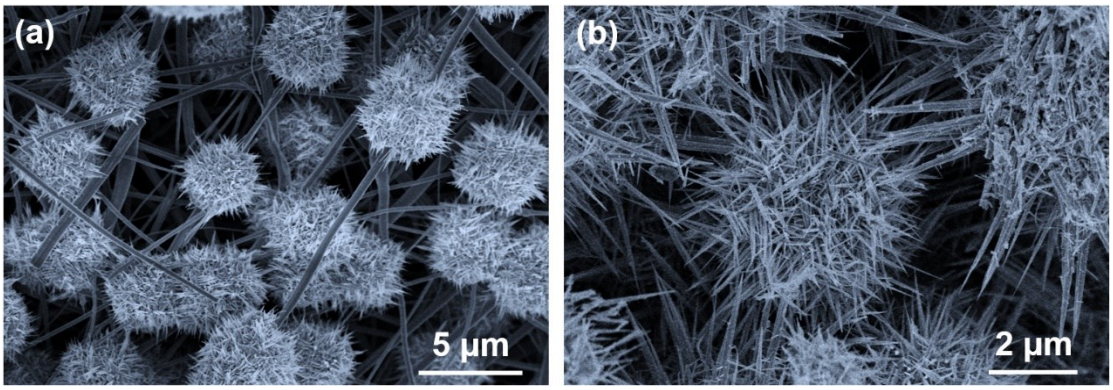

Figure S10. (a) Low- and (b) high-magnification SEM images of P-doped WO_3@TiO_2 nanofibrous membrane after 12 h electrolysis at –0.55 V vs. RHE.

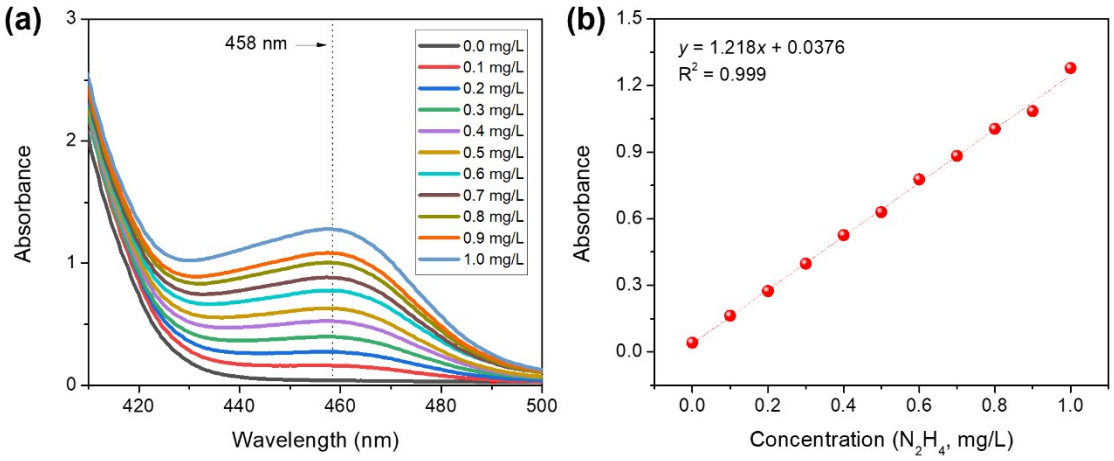

Figure S11. (a) UV-vis spectra and (b) calibration curve of N_2H_4 solutions with different concentrations based on the Watt and Chrisp method.

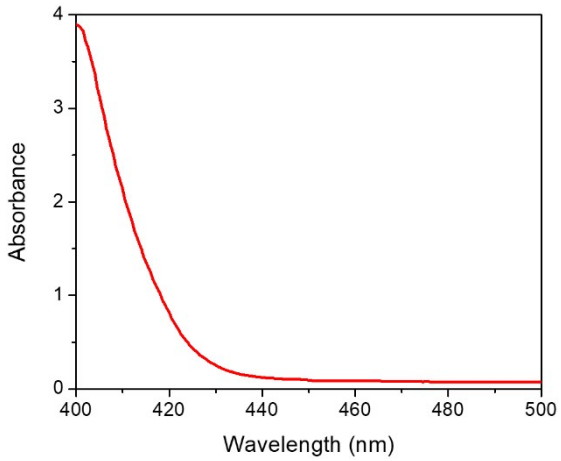

Figure S12. UV-vis spectra of the electrolyte after 12 h electrolysis in N_2 at –0.55 V *vs.* RHE (in the presence of P-WO_3@TiO_2 nanofibrous membrane).

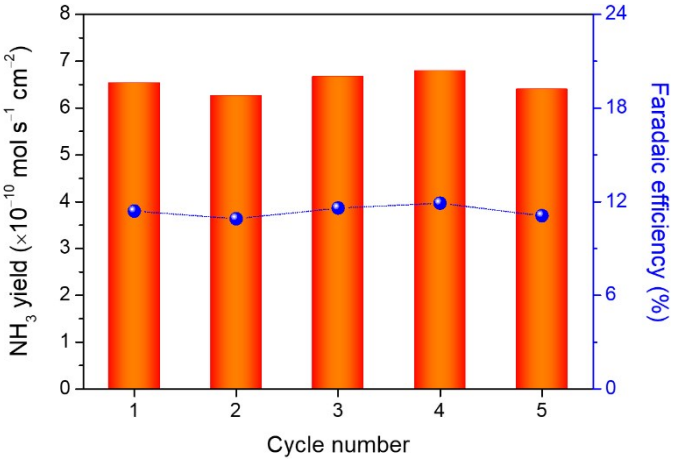

Figure S13. Recycling results of P-WO_3@TiO_2 nanofibrous membrane at –0.55 V *vs.* RHE.

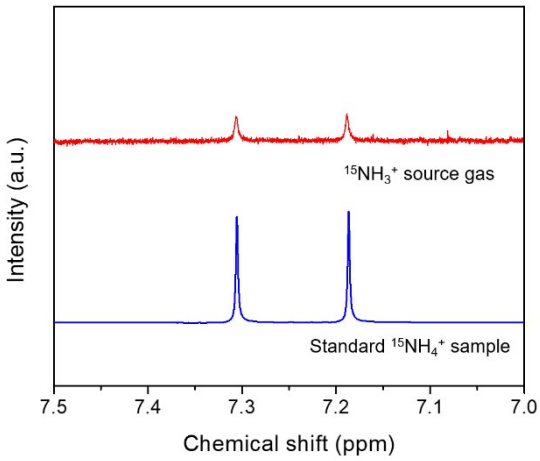

Figure S14. ^{1}H NMR spectra of standard $^{15}NH_4^+$ sample and $^{15}N_2$-saturated electrolyte after electrolysis at –0.55 V *vs.* RHE for 12 h.

Table S1. Comparison of NRR performances of P-WO_3@TiO_2 nanofibrous membrane and recently reported, heteroatom-doped transition metal electrocatalysts.

Catalyst	Electrolyte	Testing method	V_{NH3}	FE	Reference
P-doped WO_3@TiO_2 nanofibrous membrane	0.1 M Na_2SO_4	Indophenol blue method	6.54×10^{-10} mol s^{-1} cm^{-2}	17.5%	**This work**
Cu-doped TiO_2 nanoparticles on carbon paper	0.5 M $LiClO_4$	Indophenol blue method	21.31 μg h^{-1} mg^{-1}	21.99%	*Adv. Mater.* 2020, **32**, 2000299
Mo-doped MnO_2 nanoflowers on carbon cloth	0.1 M Na_2SO_4	Indophenol blue method	36.6 μg h^{-1} mg^{-1}	12.1%	*Appl. Catal. B: Environ.* 2020, **264**, 118525
Mo-doped SnS_2 nanosheets on carbon cloth	0.5 M $LiClO_4$	Indophenol blue method	41.3 μg h^{-1} mg^{-1}	20.8%	*J. Mater. Chem. A* 2020, **8**, 7117
Zr-doped TiO_2 nanotubes on carbon paper	0.1 M KOH	Indophenol blue method	8.9 μg h^{-1} cm^{-2}	17.3%	*Nat. Commun.* 2019, **10**, 2877
C-doped TiO_2 nanoparticles on carbon paper	0.1 M $LiClO_4$	Indophenol blue method	14.8 μg h^{-1} mg^{-1}	17.8%	*Angew. Chem. Int. Ed.* 2019, **58**, 13101
V-doped TiO_2 nanorods on carbon paper	0.5 M $LiClO_4$	Indophenol blue method	17.73 μg h^{-1} mg^{-1}	15.3%	*Small Methods* 2019, **3**, 1900356
Fe-doped TiO_2 nanoparticles on carbon paper	0.5 M $LiClO_4$	Indophenol blue method	25.47 μg h^{-1} mg^{-1}	25.6%	*Angew. Chem. Int. Ed.* 2019, **58**, 18449
Fe doped $W_{18}O_{49}$ nanowires on carbon paper	0.25 M $LiClO_4$	Indophenol blue method	24.7 μg h^{-1} mg^{-1}	20.0%	*Angew. Chem. Int. Ed.* 2020, **59**, 7356
OV-rich TiO_2 nanosheets on carbon paper	0.1 M HCl	Indophenol blue method	3.0 μg h^{-1} mg^{-1}	6.5%	*Appl. Catal. B: Environ.* **2019**, *257*, 117896
Fe-doped CeO_2 nanosheets on carbon cloth	0.5 M $LiClO_4$	Indophenol blue method	26.2 μg h^{-1} mg^{-1}	14.7%	*J. Mater. Chem. A* 2020, **8**, 5865
B-doped MnO_2 nanosheets on carbon cloth	0.5 M $LiClO_4$	Indophenol blue method	54.2 μg h^{-1} mg^{-1}	16.8%	*J. Mater. Chem. A* 2020, **8**, 5200
B-doped VS_2 nanosheets on carbon cloth	0.5 M $LiClO_4$	Indophenol blue method	55.7 μg h^{-1} mg^{-1}	16.4%	*J. Mater. Chem. A* 2020, **8**, 16195
P-doped V_2O_3/C nanoneedles on carbon paper	0.1 M Na_2SO_4	Indophenol blue method	12.6 μg h^{-1} mg^{-1}	6.06%	*ChemNanoMat* 2020, **6**, 1315