Electronic Supplementary Information

Experimental section

Materials: V_2O_5, $H_2C_2O_4\cdot 2H_2O$, urea, $N_2H_4\cdot H_2O$ and C_2H_5OH were bought from Beijing Chemical Corporation. p-$C_9H_{11}NO$, $C_7H_6O_3$, $C_6H_5Na_3O_7\cdot 2H_2O$, and $C_5FeN_6Na_2O\cdot 2H_2O$ was purchased from Aladdin Ltd. (Shanghai, China). CC was provided by Hongshan District, Wuhan Instrument Surgical Instruments business. All the reagents were used as received. The water used throughout all experiments was purified through a Millipore system.

Preparation of V_2O_5/CC and VN/CC: The V_2O_5 nanowire array precursor was synthesized by hydrothermal route. In a typical synthesis, the V_2O_5 powders (100 mg) and oxalic acid ($H_2C_2O_4\cdot 2H_2O$, 170 mg) were added into 25 mL distilled water under continuous stirring until a clear solution were formed. 60 mg urea and 5 mL ethylene glycol were added with stirring 30 min, and then transferred into 50 mL Teflon-lined stainless steel autoclave liners with a piece of CC. The autoclave was maintained at 180 ^oC for 12 h, and then allowed to cool down. The CC with precursor was washed with deionized water several times and dried in oven. The V_2O_5/CC was obtained by annealing in air at 350 °C for 2 h. To make VN/CC, V_2O_5/CC was placed in the furnace and heated to 800 °C with a heating speed of 5 °C min^{-1} under a flowing NH_3 atmosphere. After reacting 3 h at 800 °C, the system was allowed to cool down to room temperature naturally still under a flowing NH_3 atmosphere. Before measurement, VN/CC was immersed in 0.1 M HCl for 2 h to remove the NH_3 on the surface of VN.

Characterizations: XRD measurements were performed using a LabX XRD-6100 X-ray diffractometer with Cu Kα radiation (40 kV, 30 mA) of wavelength 0.154 nm (SHIMADZU, Japan). SEM measurements were carried out on a XL30 ESEM FEG scanning electron microscope at an accelerating voltage of 20 kV. TEM images were collected on a Zeiss Libra 200FE transmission electron microscope operated at 200 kV. XPS measurements were performed using an ESCALABMK II X-ray photoelectron spectrometer with the exciting source of Mg.

Electrochemical measurements: Electrochemical measurements were performed with a CHI 660E electrochemical analyzer (CH Instruments, Inc., Shanghai) using a standard three-electrode system using VN/CC as working electrode, graphite rod as the counter electrode, and a saturated Ag/AgCl used as the reference electrode. Before measAll potentials measured were calibrated to RHE using the following equation: E (RHE) = E (Ag/AgCl) + 0.059 × pH + 0.197 (V). Polarization curves were obtained using linear sweep voltammetry with a scan rate of 20 mV s^{-1} and were the steady-state ones after several cycles. All experiments were carried out at room temperature (~ 25 °C). For N_2 reduction experiments, the HCl electrolyte was purged with N_2 for 30 min before the measurement. Potentiostatic test was conducted in N_2 saturated 0.1 M HCl solution (30 mL) in a two-compartment cell, which was separated by Nafion membrane.

Determination of ammonia: Concentration of produced ammonia was spectrophotometrically determined by the indophenol blue method. In detail, 2 mL the electrolyte was removed from the electrochemical reaction vessel, and added into 2 mL 1.0 M NaOH solution containing salicylic acid and sodium citrate. And then, 1 mL 0.05 M NaClO and 0.2 mL 1 wt % $C_5FeN_6Na_2O$ were also added into the above solution. After standing at room temperature for 2 h, the UV-Vis absorption spectrum was measured. The concentration of indophenol blue was determined using the absorbance at wavelength of 655 nm. The concentration-absorbance curves were calibrated using standard ammonia chloride solution with a serious of concentrations. The fitting curve ($y = 0.365x + 0.083$, $R^2=0.999$) shows good linear relation of absorbance value with NH_3 concentration by three times independent calibrations.

Determination of hydrazine: The hydrazine present in the electrolyte was estimated by the method of Watt and Chrisp. A mixture of p-$C_9H_{11}NO$ (5.99 g), HCI (concentrated, 30 mL) and C_2H_5OH (300 mL) was used as a color reagent. In detail, 5 mL electrolyte was removed from the electrochemical reaction vessel, and added into 5 mL above prepared color reagent, then standing 10 min at room temperature. The absorbance of the resulting solution was measured at 455 nm. The concentration-absorbance curves were calibrated using standard $N_2H_4 \cdot H_2O$ solution with a serious of concentrations. The fitting curve ($y = 0.575x + 0.035$, $R^2=0.999$) shows good linear relation of absorbance value with N_2H_4 concentration by three times independent calibrations.

Faradaic efficiency: The rate of ammonia formation was firstly calculated using the following equation: $vNH_3 = (cNH_3 \times V)/(17 \times t \times A)$, Where cNH_3 is the measured NH_3 concentration, V is the volume of electrolyte, t is the reduction reaction time and A is the effective area of the cathode. Assuming three electrons were needed to produce one NH_3 molecule, the Faradaic efficiency can be calculated as follows: Faradaic efficiency = $(3F \times cNH_3 \times V)/(17 \times Q)$, where F is the Faraday constant and Q is the quantity of applied electricity.

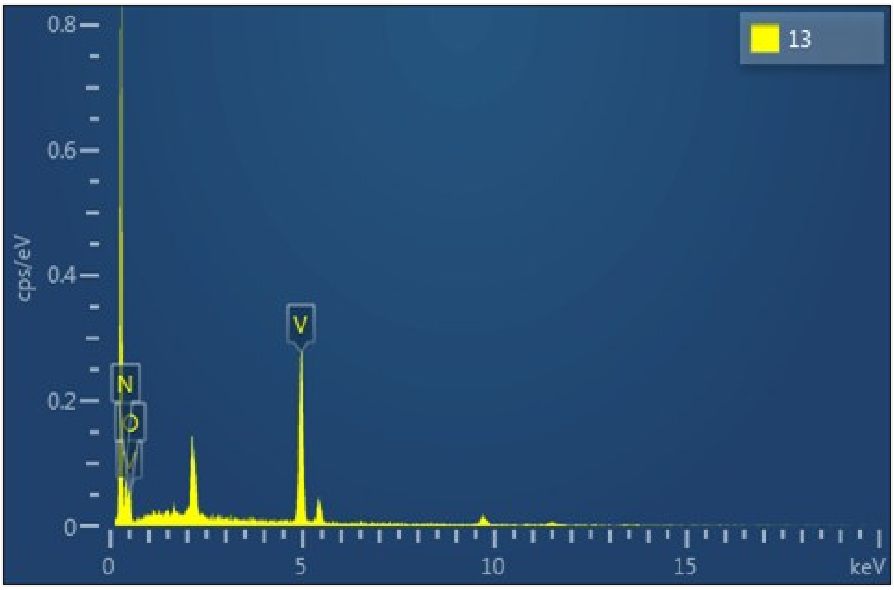

Fig. S1. EDX spectrum of VN/CC.

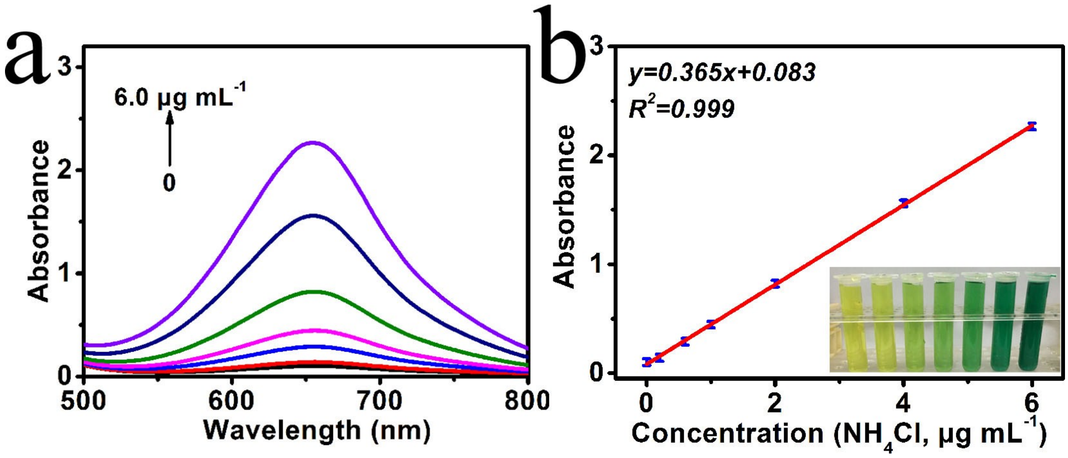

Fig. S2. (a) UV-Vis absorption spectra of indophenol assays with NH_4^+ ions after incubated for 2 h at room temperature. (b) Calibration curve used for estimation of NH_3 by NH_4^+ ion concentration.

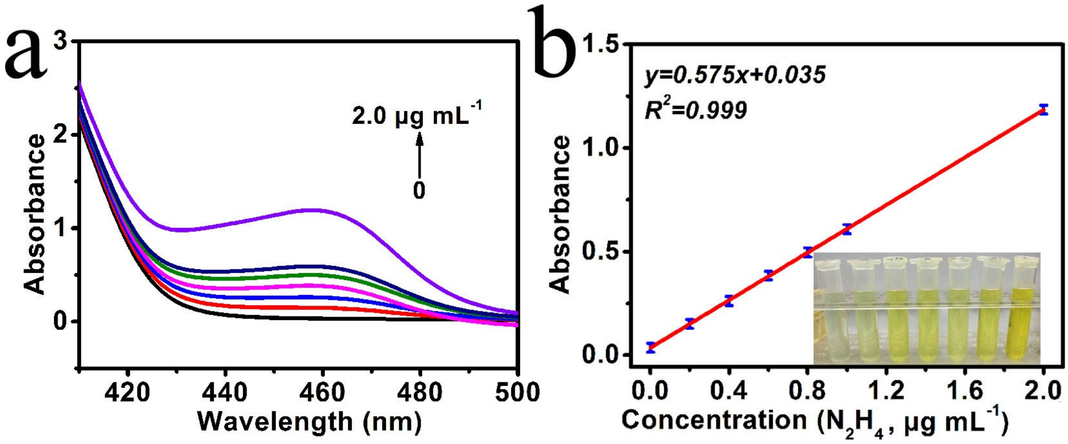

Fig. S3. (a) UV-Vis absorption spectra of various $N_2H_4 \cdot H_2O$ concentrations after incubated for 10 min at room temperature. (b) Calibration curve used for estimation of N_2H_4 concentration.

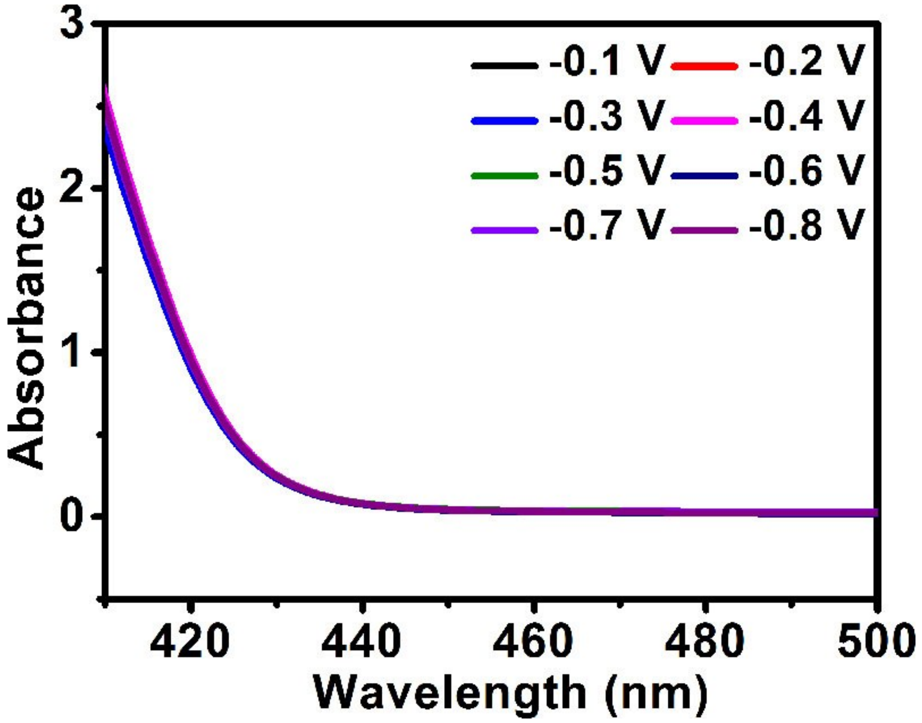

Fig. S4. (a) UV–Vis absorption spectra of the electrolytes stained with indophenol indicator after VN/CC electrolysis at different potentials for 3 h.

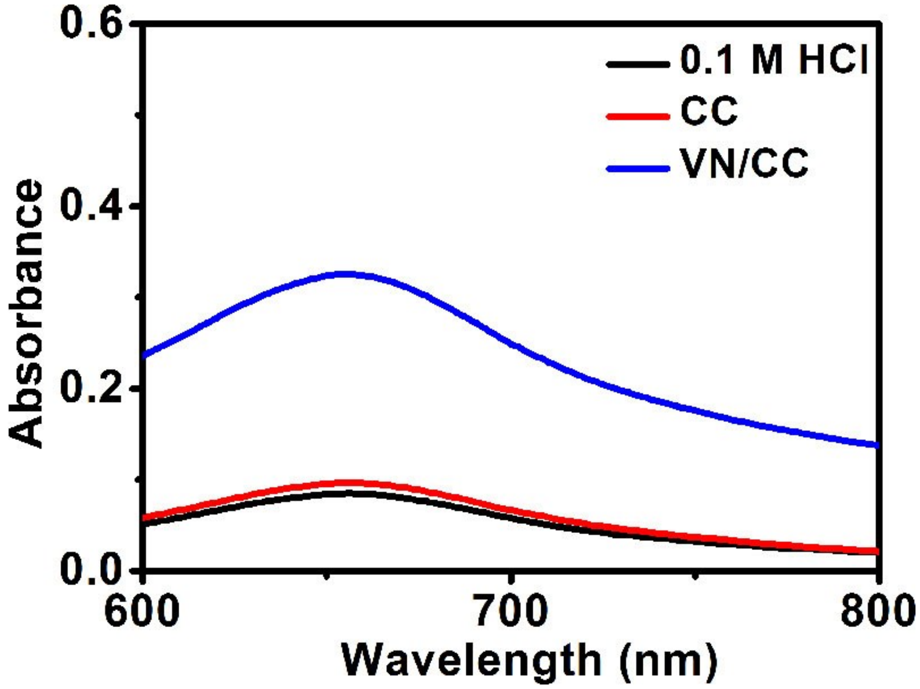

Fig. S5. (a) UV-Vis absorption spectra of the electrolytes stained with indophenol indicator before and after 3 h electrolysis at -0.3 V versus RHE at room temperature.

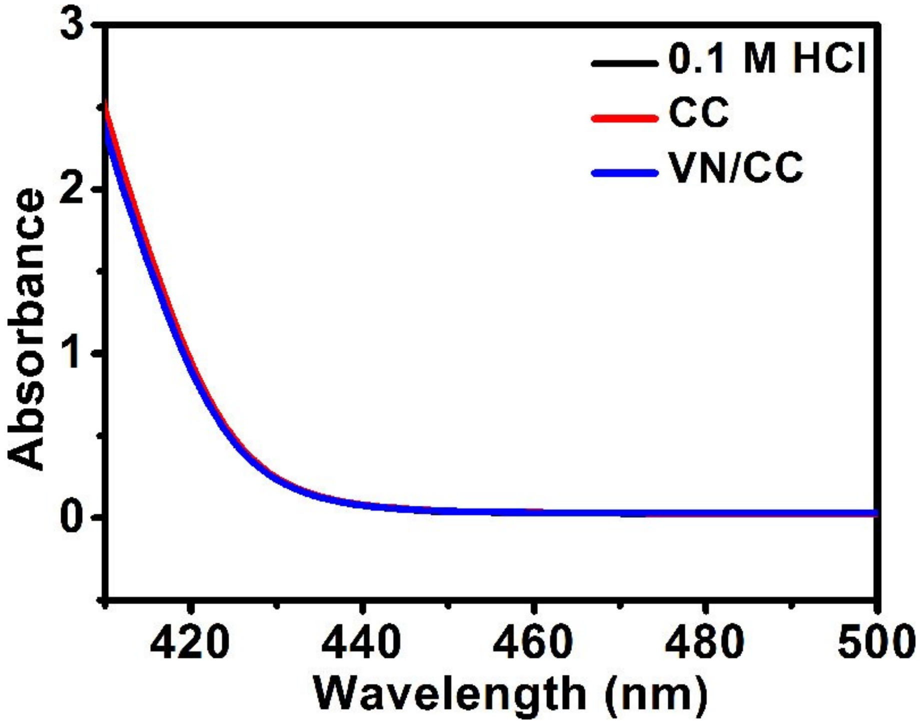

Fig. S6. (a) UV-Vis absorption spectra of the electrolytes estimated by the method of Watt and Chrisp before and after 3 h electrolysis in N_2 atmosphere at -0.3 V versus RHE at room temperature.

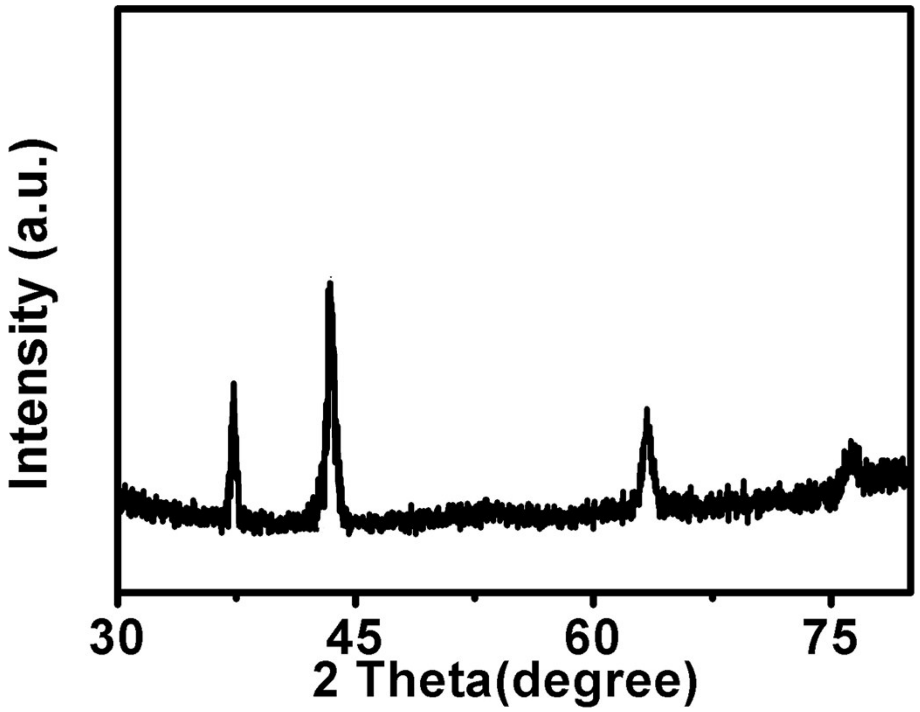

Fig. S7. The XRD pattern of VN after test.

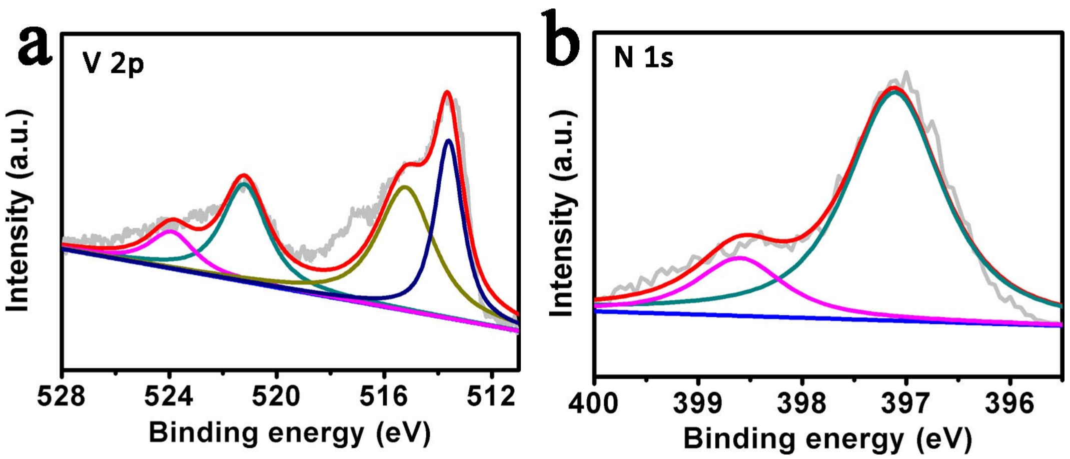

Fig. S8. XPS spectra of VN in the (a) V 2p and (b) N 1s regions after test.