

Supplementary Information

Electrochemical nitrogen reduction to ammonia at ambient conditions on nitrogen and phosphorus co-doped porous carbon

Pengfei Song*, Hao Wang, Li Kang, Baocheng Ran, Honghong Song and Rongmin Wan

Key Laboratory of Eco-Environment-Related Polymer Materials of Ministry of Education, Key Laboratory of Polymer Materials of Gansu Province, Gansu International Scientific and Technological Cooperation Base of Water-Retention Chemical Functional Materials, College of Chemistry and Chemical Engineering, Northwest Normal University, Lanzhou 730070, P. R. China.

* Corresponding Emails: songpf@nwnu.edu.cn

Materials and Method

Chemicals and materials

Hydrazine monohydrate ($\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$, Aladdin, 98.0%), Sodium hypochlorite (NaClO , Aldrich, 99%), sodium citrate (99%), N_2 gas (99.99%), Ar gas (99.99%), salicylic acid (Sinopharm Chemical Reagent Co. Ltd., 99.5%), sodium nitroferricyanide ($\text{Na}_2[\text{Fe}(\text{NO})(\text{CN})_5]$, Aldrich 99%), para-(dimethylamino) benzaldehyde (Shanghai Zhongqin Chemical Reagent Co. Ltd., 99.9%), phytic acid solution (TCI, 50 wt % aqueous solution) was diluted to 16% aqueous solution. Acetone (99.5%), hydrochloric acid (36-38%) and ammonium chloride (NH_4Cl , 99.5%) was obtained from Beijing Chemical Works. Ethanol absolute (99.7%), sodium carbonate (99.8%), ammonium persulphate (99%) and sodium hydroxide (NaOH , 96%) was purchase from Sinopharm Chemical Reagent Co. Ltd., phenol and aniline (99.5%) was purchase from Shanghai Chemical Works. Nafion (DuPont, D520, 5 wt %) was diluted to 0.05% aqueous solution. 5L of $^{15}\text{N}_2$ gas in cylinder (WUHAN NEWRADAR SPECIAL GAS CO., LTD., Purity 99%).

Preparation of catalyst

N, P co-doped carbon mater (NPC) was pyrolysed by polyaniline (PANi) aerogels.¹ Firstly, aniline monomer was added into phytic acid solution (16%, wt/wt in water). Ammonium persulphate (APS, 0.96 g) was dissolved in 10 mL deionized water under stirring. After cooling down to about 4 °C, both solutions were mixed together and then kept one night without stirred. The resultant hydrogel was washed by immersion in deionized water for two days then freeze-dried for 24 h to obtain PANi aerogels. The NPC was obtained by calcining the PANi at the desired temperatures of 900 °C for 2 h under argon.

Physicochemical characterization

X-ray photoelectron spectroscopy (XPS) measurements were carried out using a Physical Electronics PHI-5702 spectrometer with Al $\text{K}\alpha$ X-ray as radiation source. The position of the C1s peak, that is 284.4 eV, was used to correct the binding energies of all the catalysts. Nitrogen sorption isotherms were measured at -196 °C using the BET (AUTOSORB-Iq2, USA). The specific surface areas were calculated using adsorption data in a relative pressure ranging by the Brunauer-Emmett-Teller (BET) method. The pore size distribution curve was calculated by desorption branches of the isotherms using Barrett-

Joyner-Halenda (BJH) method. The morphology and microstructure of the samples were investigated by Field-Emission Scanning Electron Microscopy (FESEM, ULTRA Plus, Zeiss). Transmission electron microscopy (TEM, TECNAI G2 F20 STWIN D2278, FEI) and high-resolution TEM (HRTEM) were carried out on microscope operated at an accelerating voltage of 200 kV. The absorbance data of spectrophotometer were measured on ultraviolet-visible (UV-Vis, Unicosh UV-2800) spectrophotometer. ^1H NMR spectra were obtained in D_2O -DMSO (Bruker DRX-600 NMR). Nexus 870 spectrometer (Nicolet) equipped with a liquid-nitrogen-cooled MCT-A detector and an EverGlo IR source were used to measure the in situ FTIR spectroscopic of the electrochemical. MS studies were carried on an Agilent 6520B Q-TOF. The gas was measured by gas chromatography (GC 9560, Shanghai Huaai Chromatography Analysis Co., Ltd.).

Electrode preparation

The 28.4 mg N, P co-doped carbon powders was dispersed in 500 μL Nafion solution with ultrasonically for 30 min to produce the homogeneous catalyst ink. Then transfer 10 μL of catalyst solution onto the glassy carbon electrode surface (GC XR303, $D = 3$ mm, Xianren Instrumentation, Shanghai) and dried in the air for 1 h served as a working electrode.

Electrochemical measurements

The electrochemical experiments were carried out with an electrochemical workstation by using a three-electrode configuration which including working electrode, Pt wire and Ag/AgCl (in saturated KCl solution) were used as the working electrode, counter electrode and reference electrode, respectively. The electrolyte is 0.1 M HCl solution ($\text{pH} = 1$). The potential was controlled by an autolab potentiostat/galvanostat (CHI660E). All potentials were measured against an Ag/AgCl reference electrode and converted to the RHE reference scale using E (vs. RHE) = E (vs. Ag/AgCl) + 0.197 V + $0.0591 \times \text{pH}$. In the NRR process, a constant potential test was performed in the N_2 gas saturated dilute hydrochloric acid electrolyte (30 mL), which was passed into nitrogen for 30 minutes before measurement, and the N_2 gas was continuously fed into the electrolyte with a flow rate of 10 mL/min.

Electrochemical in Situ FTIR Reflection Spectroscopy measurements

The electrolyte was passed into N_2 gas for 30 minutes before measurement, and the N_2 gas was continuously fed into acid electrolyte. All experiments were carried out at room temperature. Nexus 870 spectrometer (Nicolet) equipped with a liquid-nitrogen-cooled MCT-A detector and an EverGlo IR

source were used to measure the in-situ FTIR spectroscopic of the electrochemical.² The IR window was a CaF₂ disk, before FTIR measurement, the IR cell with a thin layer configuration which between the electrode and the IR window was obtained by pushing the electrode against the window,³ infrared radiation sequentially passed through the CaF₂ window and the thin-layer solution, and reflected from the electrode surface. We use both single potential alteration FTIR spectroscopy (SPAFTIRS) and time resolved SPAFTIR spectroscopy (TRFTIR) procedures to collect in situ FTIR spectra. It took about 100 s that 200 singlebeam spectra were collected and coded for each resulting spectrum. The spectral resolution was 8 cm⁻¹. The resulting spectra were reported as the relative change in reflectivity and calculated as $\Delta A = -\log[R(E_1)/R(E_2)]$, ΔA is relative absorbance, $R(E_1)$ and $R(E_2)$ are the electrode reflectivity at potentials E_1 and E_2 (reference), respectively.

Determination of ammonia and hydrazine hydrate

The content of ammonia in the electrolyte after the reaction was measured by the indophenol blue method⁴ with some modification. 2 mL aliquot of the electrolyte was removed to color comparison tube, and add 2 mL 1 M NaOH solution containing salicylic acid and sodium citrate, 0.2 mL of 1 wt % sodium nitroferricyanide (Na₂[Fe(NO)(CN)₅]) and 1 mL of 0.05 M NaClO, standing at room temperature for 2 h, and then to measuring the UV-Vis absorption spectrum of the solution. The hydrazine present in the electrolyte was estimated by the method of Watt and Chrisp.⁵ A mixture of para-(dimethylamino) benzaldehyde (5.99 g), HCl (concentrated, 30 mL) and ethanol (300 mL) was used as a color reagent. First, preparing a series of reference solutions, by pipetting suitable volumes of the hydrazine hydrate-nitrogen 0.1 M HCl solution in colorimetric tubes; second, making up to 5 mL with diluted hydrochloric acid electrolyte (pH = 1); third, adding 5 mL above prepared color reagent and stirring 10 min at room temperature. Fourth, the absorbance of the resulting solution was measured at 455 nm, and the yields of hydrazine were estimated from a standard curve using 5 mL electrolyte and 5 mL color reagent.

Isotopic labeling experiments

¹⁵N₂ gas (WUHAN NEWRADAR SPECIAL GAS CO., LTD., Purity 99%) was used as received. The potentiostatic NRR at -0.2 V vs. RHE is measured at room temperature and atmospheric pressure with continuous ¹⁵N₂ stream to the cathode and the employed electrolyte is HCl solution (0.1M). After NRR, the product was collected by freeze-drying of the electrolyte. The product stained with indophenol indicator was measured by LC-MS technique, the method as follows⁶: 0.5 mL aliquot was mixed with

0.1 mL of 1% phenolic solution in 95% ethanol, 0.375 mL of 1% NaClO in alkaline Na-citrate solution in water and 0.5 mL of 0.5% Na₂[Fe(NO)(CN)₅] in water, standing at room temperature for 2 h before testing. MS studies were carried on an Agilent 6520B Q-TOF (LC-MS).

Determination Hydrogen evolution reaction

The hydrogen production experiments were performed in a gastight electrochemical cell, the solution was 0.1 M HCl solution with the NPC as the working electrode. Before the test, the exclusion of air by bubbling with high purity N₂ was performed for around 30 min. Hydrogen gas evolution was measured by gas chromatography (GC 9560, nitrogen as a carrier gas) with thermal conductivity detection (TCD).

Table S1. Element compositions of PANi aerogel and NPC samples from XPS.

Sample	C %	N %	O %	P %
PANi	51.2	7.0	36.6	5.2
NPC ^a	78.1	3.6	15.0	3.3
NPC ^b	77.2	3.2	17.3	2.3

^aThe XPS measurement before NRR; ^bThe XPS measurement after NRR.

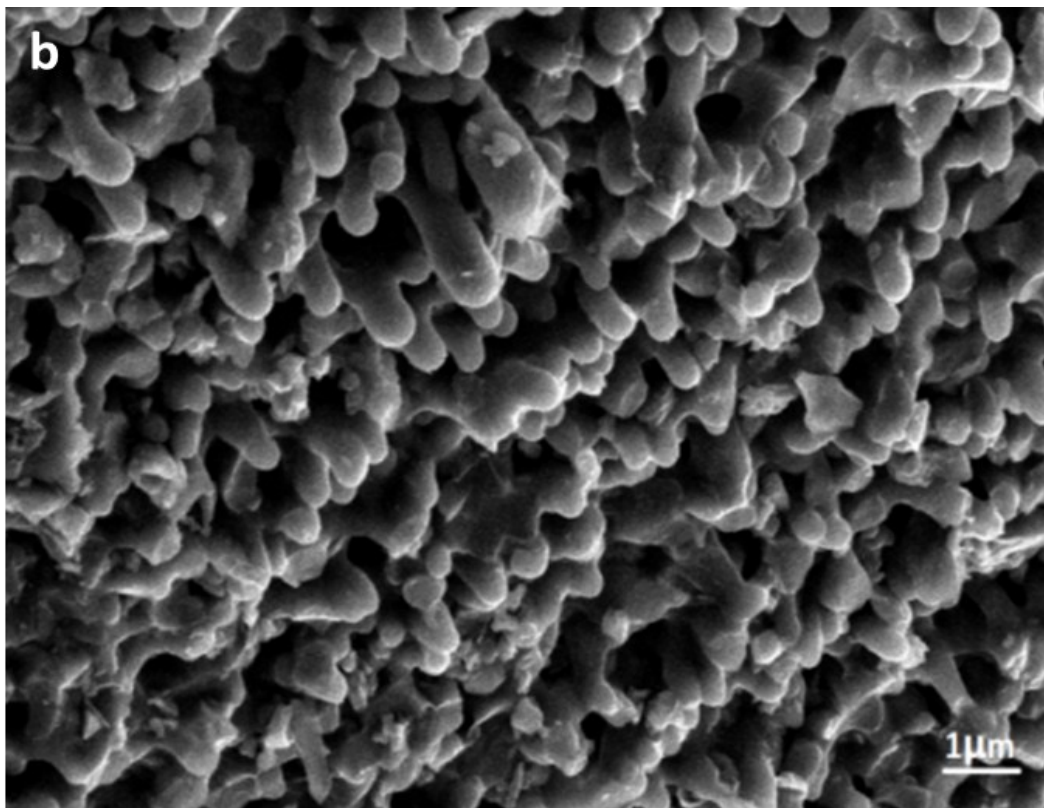
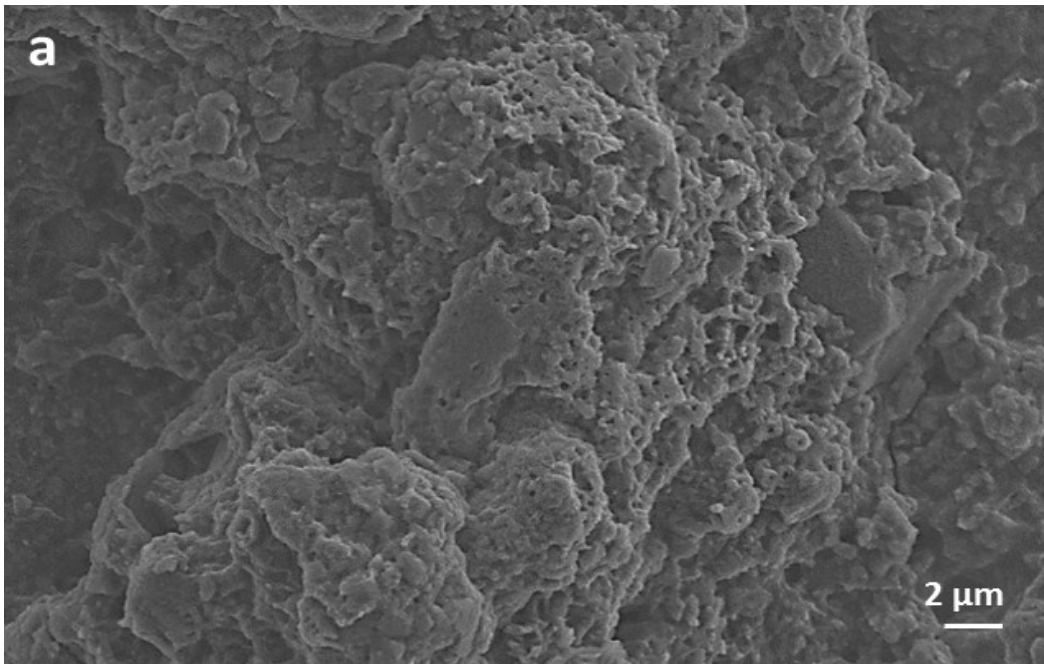


Fig. S1. SEM images of (a) PANi and (b) NPC.

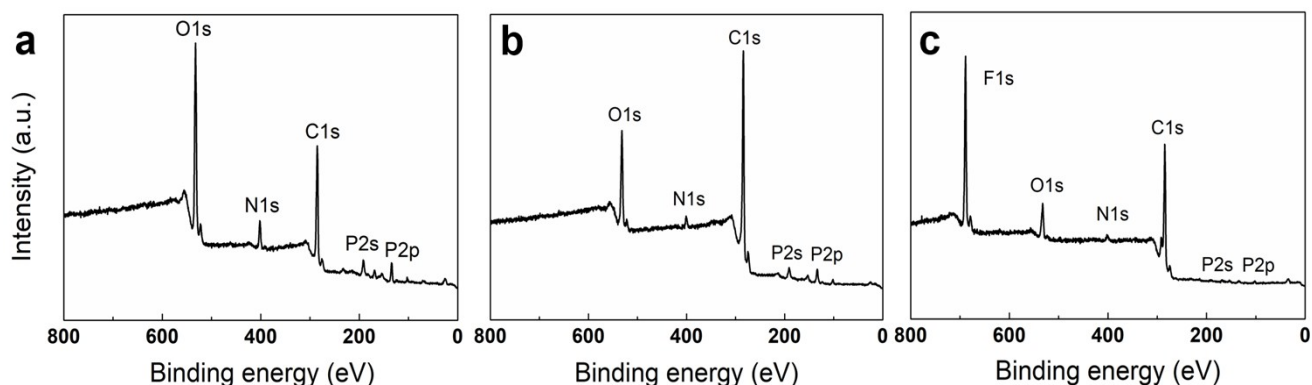


Fig. S2. XPS survey spectra of (a) PANi aerogel and NPC (b) before and (c) after NRR.

The XPS survey spectra shows typical C, N, P and O peaks (Fig. S2). The O peak in the PANi is higher than that of NPC (Fig. S2a). During the pyrolysis of PANi aerogel, the O species decline sharply (Fig. S2b), and eventually forms a carbon-based material of the NPC. As shown in Fig. S2c, the P peak of NPC is significantly decreased after NRR, indicating the loss of P species from NPC in the NRR process. Moreover, The F1s peak is clearly observed in Fig. S2c, which can be attributed to the F species of the residual Nafion adhered to the surface of NPC after NRR.

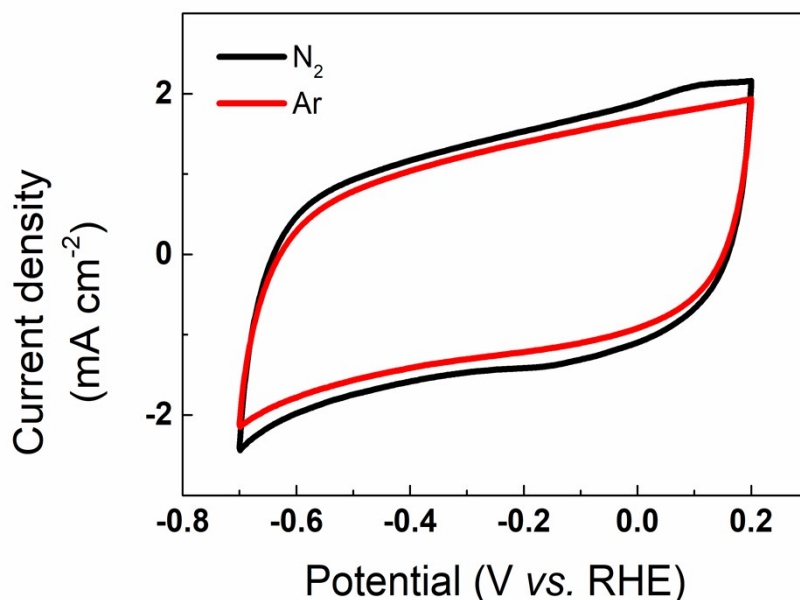


Fig. S3. Typical cyclic voltammograms in an aqueous solution of 0.1 M HCl saturated by nitrogen or argon gas at the NPC electrode.

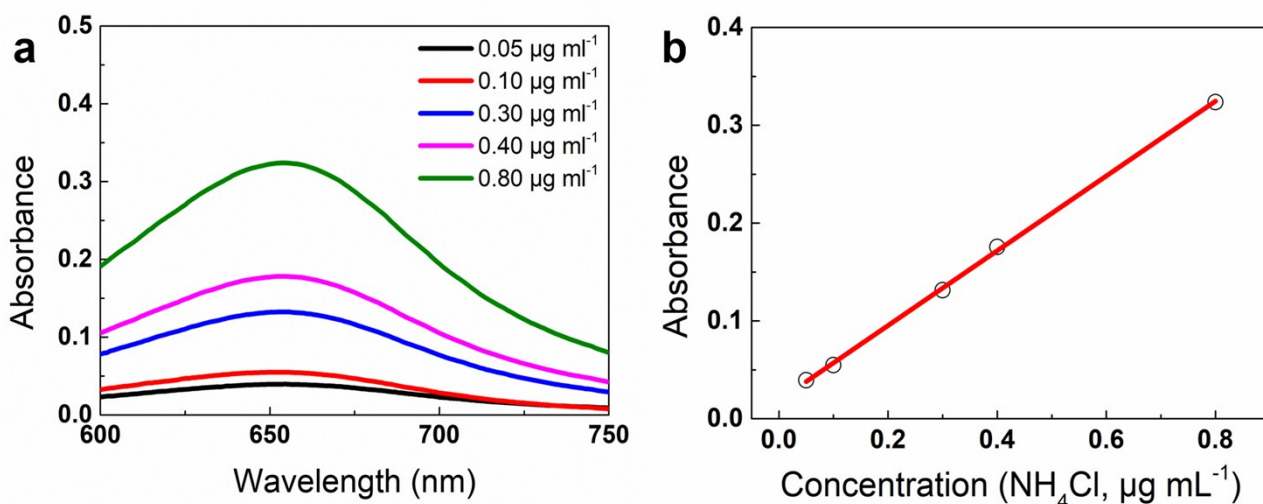


Fig. S4. Absolute calibration of the indophenol blue method using ammonium chloride solutions of known concentration as standards. (a) UV-Vis curves of indophenol assays with NH_4^+ ions; (b) calibration curve used for estimation of NH_3 by NH_4^+ ion concentration. The absorbance at 655 nm was measured on a UV-Vis spectrophotometer, and the fitting curve shows good linear relation of absorbance with NH_4^+ ion concentration ($y = 0.382x + 0.019$, $R^2 = 0.999$).

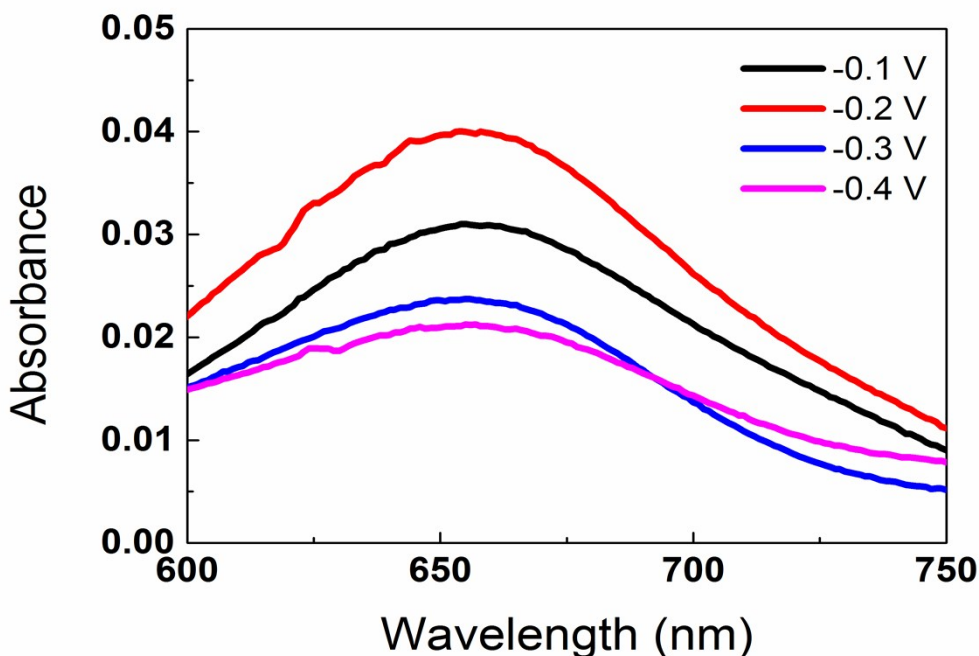


Fig. S5. UV-Vis absorption spectra of the HCl electrolyte after electrolysis on the NPC electrode stained with indophenol indicator after charging at different potentials vs. RHE for 3 h.

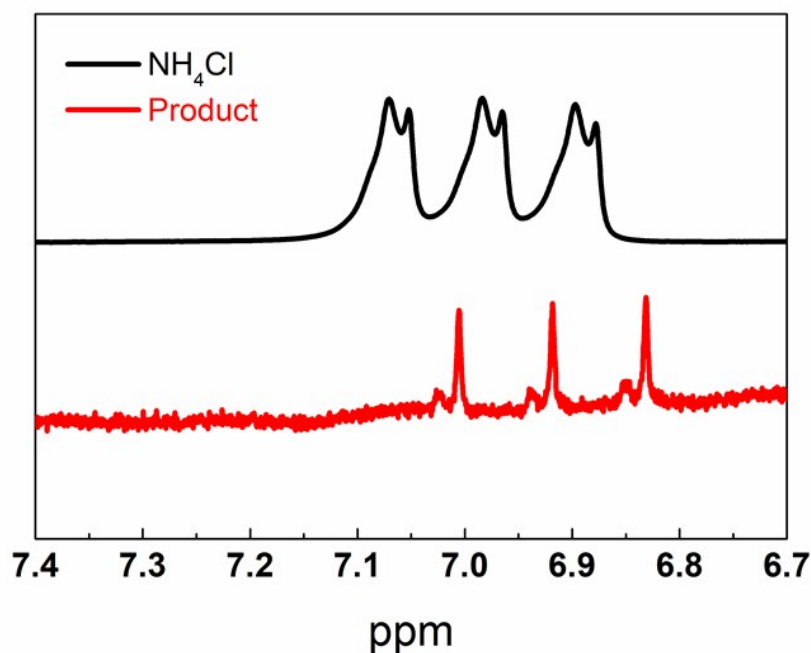


Fig. S6. The ¹H NMR spectrum of product of the experiment (red line) and standard NH₄Cl (black line).

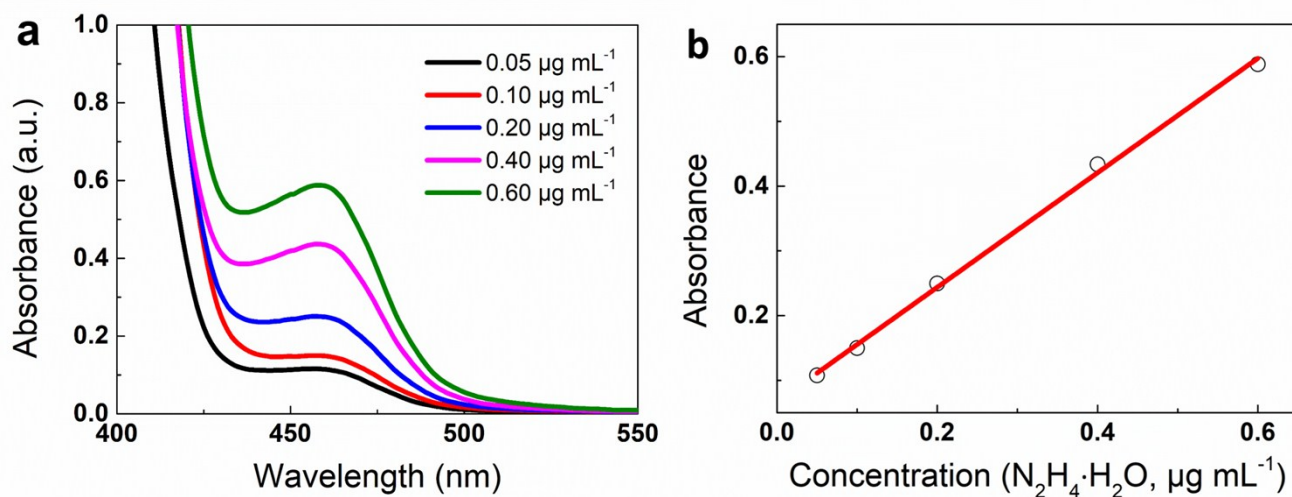


Fig. S7. Absolute calibration of the Watt and Chrisp (para-dimethylamino-benzaldehyde) method for estimating N₂H₄·H₂O concentration, using N₂H₄·H₂O solutions of known concentration as standards. (a) UV-Vis curves of various N₂H₄·H₂O concentrations after incubation for 10 min at room temperature; (b) calibration curve used for estimation of the N₂H₄·H₂O concentration. The absorbance at 455 nm was measured on a UV-Vis spectrophotometer, and the fitting curve shows good linear relation of absorbance with N₂H₄·H₂O concentration ($y = 0.884x + 0.067$, $R^2 = 0.998$) for the independent calibration curves.

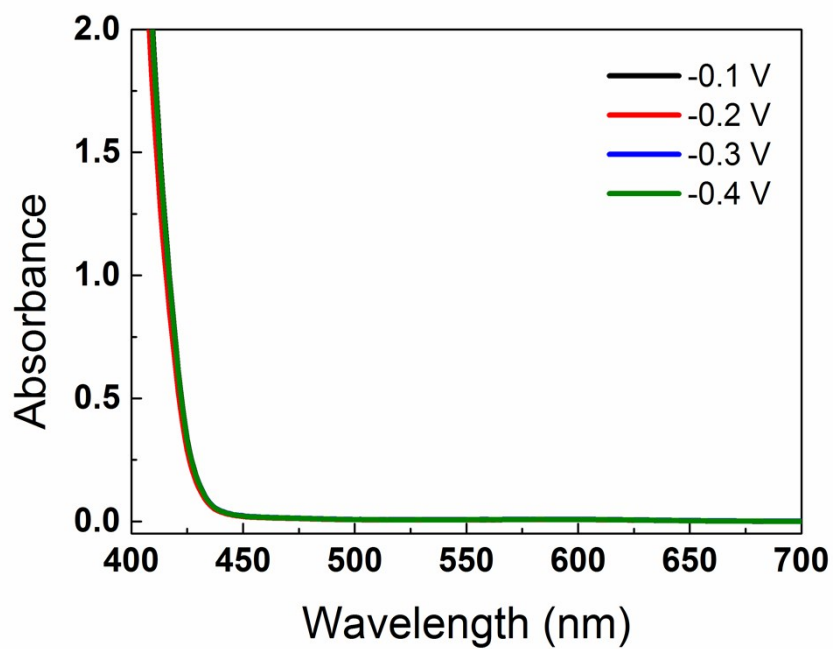


Fig. S8. UV-Vis absorption spectra of the HCl electrolyte after electrolysis on the NPC electrode stained with indophenol indicator after charging at different potentials vs. RHE for 3 h.

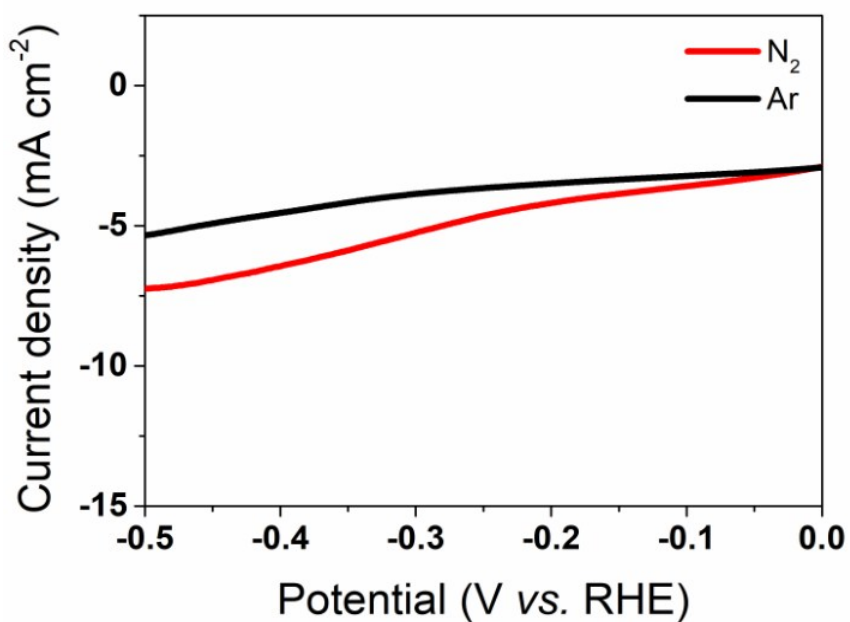


Fig. S9. Linear sweep voltammetry curves at the NPC electrode under nitrogen and argon gas.

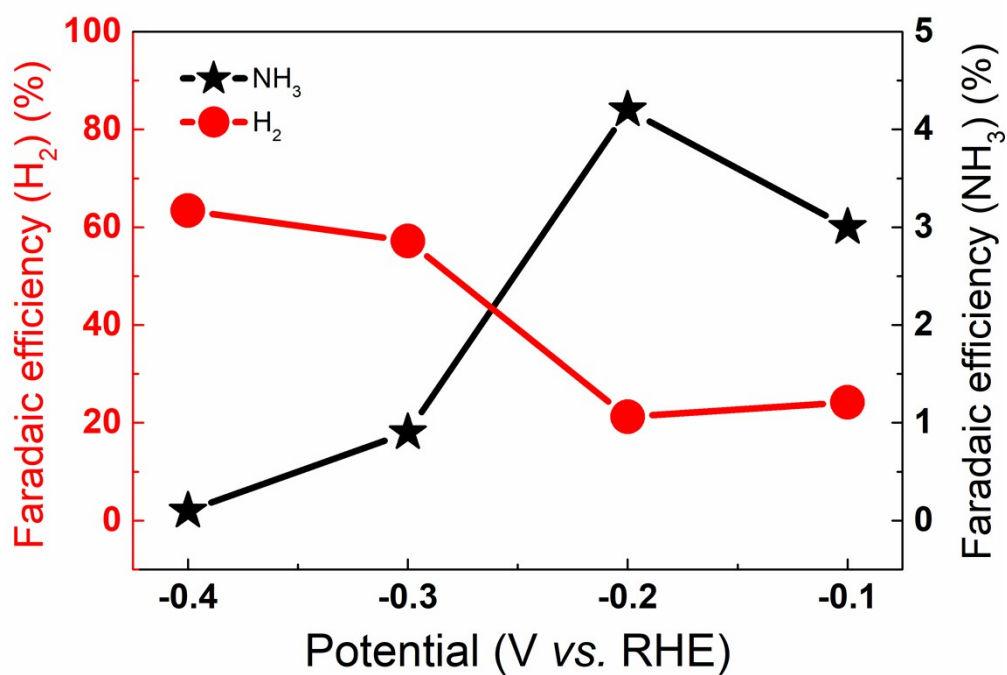


Fig. S10. Faradaic efficiency of ammonia formation and H₂ at the NPC electrode at the corresponding potential.

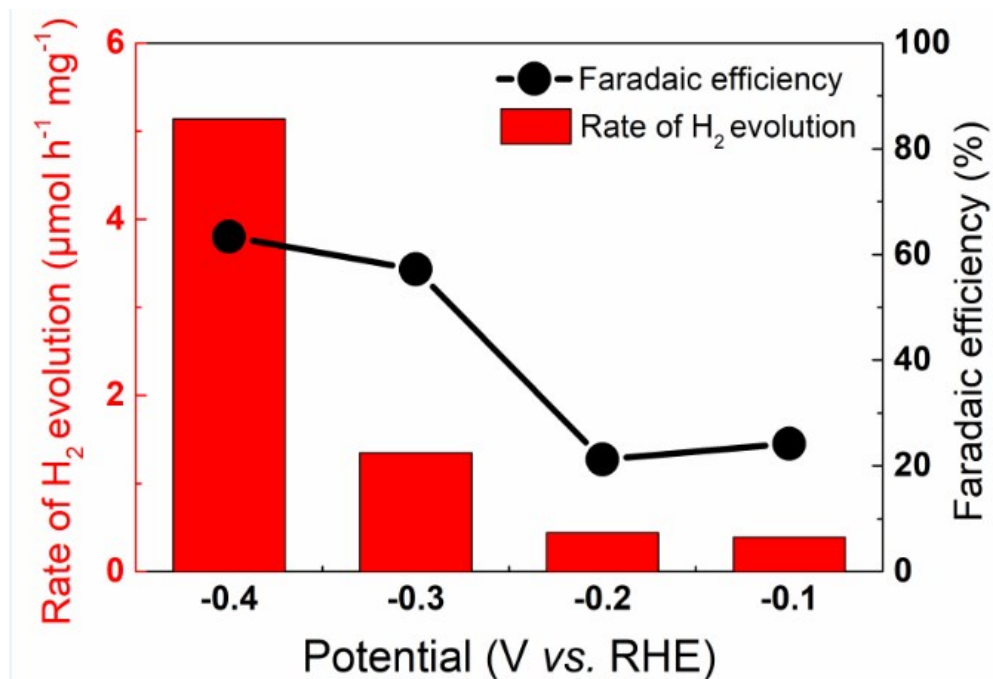


Fig. S11. Faradaic efficiency and the rate of H₂ evolution at the NPC electrode at the corresponding potential.

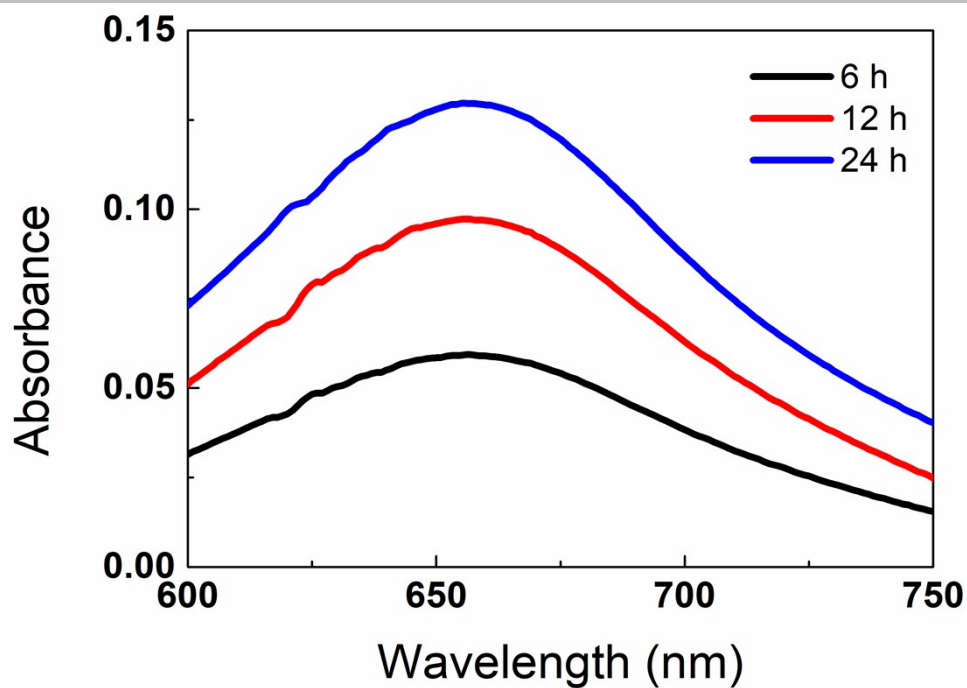


Fig. S12. UV-Vis absorption spectra of the HCl electrolyte after electrolysis on the NPC electrode stained with indophenol indicator after charging at applied potentials vs. RHE for different interval times at -0.2 V vs. RHE under N_2 gas bubbling.

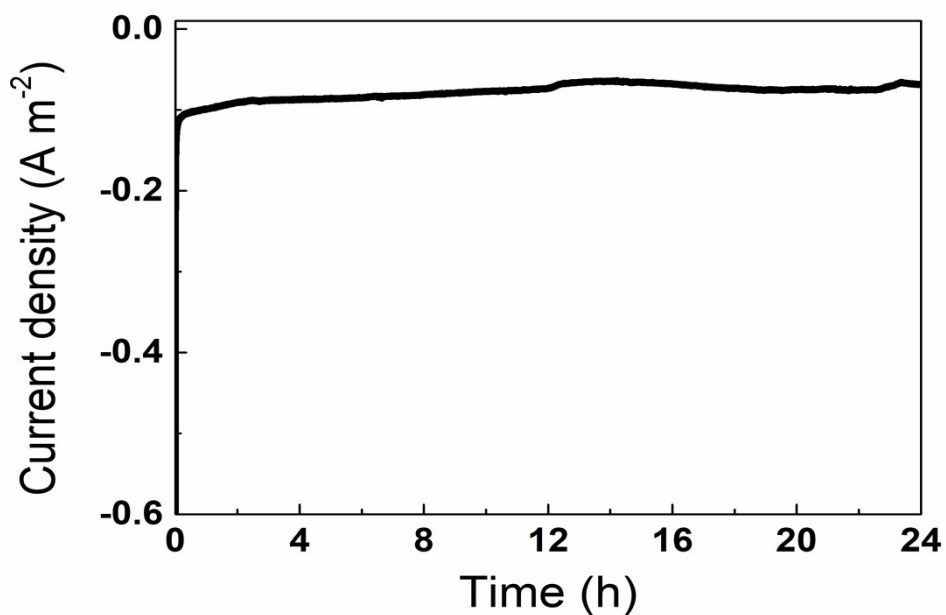


Fig. S13. Temporal behavior of the electrolysis process of the NPC electrode at the -0.2 V vs. RHE in 30 mL 0.1 M HCl electrolyte with bubbling N_2 .

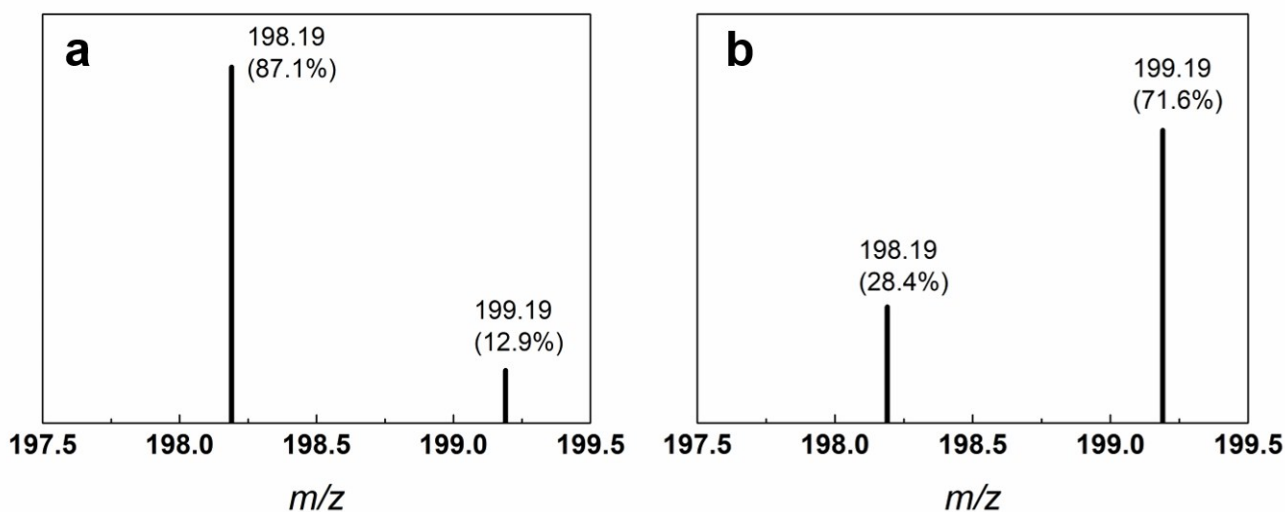


Fig. S14. LC-MS studies of indophenol assays of electrocatalysis nitrogen-fixation samples of (a) $^{14}\text{N}_2$ ($m/z = 198$) and (b) $^{15}\text{N}_2$ ($m/z = 199$).

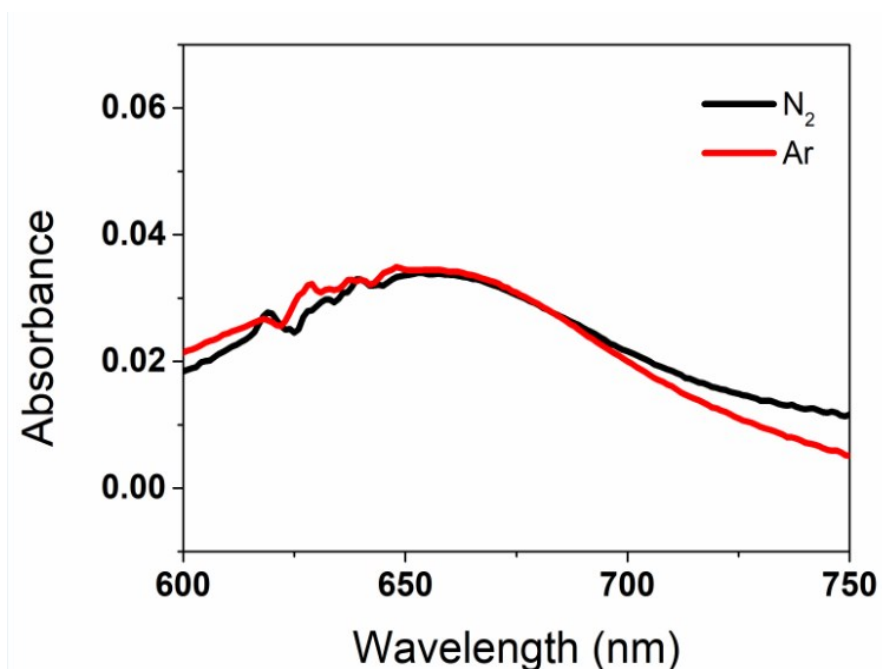


Fig. S15. UV-Vis absorption spectra of the HCl electrolyte after electrocatalysis on the NPC electrode stained with indophenol indicator. After 3 hours electrocatalysis under N_2 (black); After 6 hours electrocatalysis under Ar (red). Firstly, we test the HCl electrolyte of the NRR with bubbling N_2 in electrolyte solution after 3 hours. Then we turn off the N_2 valve immediately, the N_2 was purged from the electrochemical system by feeding Ar gas into the above electrolyte solution for around 30 min, and then we test the electrolyte of NRR with bubbling only Ar gas after 6 hours.

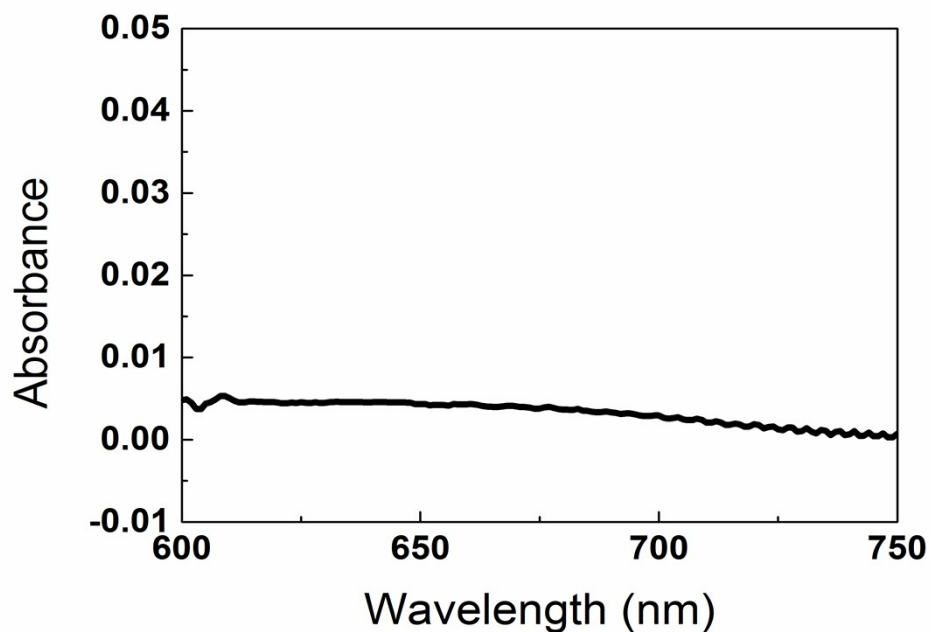


Fig. S16. UV-Vis absorption spectra of the HCl electrolyte after electrolysis on the NPC electrode stained with indophenol indicator after charging at -0.2 V vs. RHE for 3 h under Ar gas bubbling.

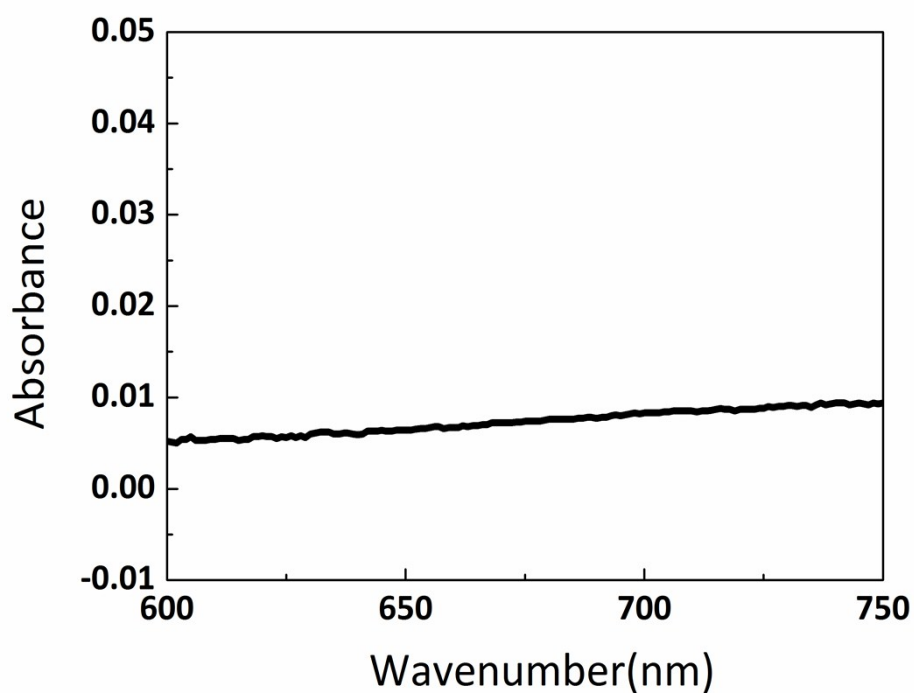


Fig. S17. UV-Vis absorption spectra of the HCl electrolyte after electrolysis on the activated carbon electrode stained with indophenol indicator after charging at -0.2 V vs. RHE for 3 h.

References

1. J. Zhang, Z. Zhao, Z. Xiao, L. Dai, *Nat. Nanotechnol.* 2015, **10**, 444 – 452.
2. M.-H. Chen, Y.-X. Jiang, S.-R. Chen, R. Huang, J.-L. Lin, S.-P. Chen, S.-G. Sun, *J. Phys. Chem. C* 2010, **114**, 19055 – 19061.
3. S.-G. Sun, D.-F. Yang, Z.-W. Tian, *J. Electroanal. Chem.* 1990, **289**, 177 – 187.
4. D. F. Bolt, *Colorimetric Determination of Nonmetals*, 1978, Vol. **2** (Wiley).
5. G. W. Watt, J. D. Crisp, *Anal. Chem.* 1952, **24**, 2006 – 2008.
6. A. Banerjee, B. D. Yuhas, E. A. Margulies, Y. Zhang, Y. Shim, M. R. Wasielewski and M. G. Kanatzidis, *J. Am. Chem. Soc.*, 2015, **137**, 2030–2034.