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Supporting Information

Hypotoxic synthesis of Co_2P nanodendrite for boosting ammonia electrosynthesis from nitrate

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Experimental Procedures

1 Materials

Table S1. All reagents and materials involved in this work.

Materials and reagents	Purity	Manufacturer
Ar	99.999%	Dalian special gases Co., Ltd., China
Anhydrous cobalt (II) dichloride ($CoCl_2$)	99.7%	Shanghai Macklin Biochemical Co., Ltd., China
Sodium chloride (NaCl)	99.5%	Shanghai Macklin Biochemical Co., Ltd., China
Aluminium chloride ($AlCl_3$)	99.0%	Shanghai Macklin Biochemical Co., Ltd., China
Phosphorus (V) pentachloride (PCl_5)	98.0%	Shanghai Aladdin Biochemical Technology Co., Ltd., China.
Alumina powder (Al, 200 mesh)	99.5%	Saen Chemical Technology (Shanghai) Co., Ltd., China.
Concentrated hydrochloric acid (HCl)	36~38%	Tianjin Fuyu Fine Chemical Co., Ltd., China.
Sodium sulphate (Na_2SO_4)	99.0%	Sinopharm Chemical Reagent Co., Ltd., China.
Sodium nitrate ($NaNO_3$)	99.0%	Sinopharm Chemical Reagent Co., Ltd., China.
RuIrOx @ Ti foam electrode	---	Kunshan Tengerhui Electronic Technology Co., Ltd., China.
Carbon black	---	Hefei Kejing Materials Technology Co., Ltd., China.
Carbon paper	---	Shanghai Hesen Electric Co., Ltd., China.

Deionized water with a resistivity of 18.23•MΩ cm was used in all experiments.

2 Synthesis and characterization of materials

Preparation of Co_2P nanostructure:

Firstly, fully mix 0.80 g PCl_5 (phosphorous source), 1.00 g $CoCl_6$ (cobalt source), and 0.32g Al powder (reductant), and then mix them evenly in the glove box filled with A to form mixture A. Secondly, mix mixture A with premixed solid molten salt (NaCl-$AlCl_3$: 2.00 g-7.14 g) to form mixture B. Finally, mixture B was sealed in a quartz glass tube and reacted for 5 h at 200 °C. After the reaction is completed, the reactor is naturally cooled to room temperature, and deionized water is added to wash the reaction products into the beaker. At this time, the molten salt is completely dissolved, and the target product is dispersed in the solution to form a suspension. In order to remove excess Al and other metal ions, dilute hydrochloric acid (volume ratio of concentrated hydrochloric acid and deionized water is 1:10), deionized water, and ethanol are used for centrifugation three times, respectively. Co_2P was finally obtained by vacuum drying at room temperature.

Materials characterization: The crystal structure of the sample was analyzed by using a desktop X-ray diffractometer (Rigaku, Japan) with Cu Kα radiation, and the scan speed was 5 °/min. The morphology and structure of the samples were further characterized by field emission scanning electron microscopy (FE-SEM, Zeiss-Sigma 300) and Field Emission transmission electron microscope (FE-TEM, Tecnai F20). The chemical state of the elements on the sample surface were obtained on X-ray photoelectron spectroscopy (XPS, Thermo Fisher (ESCALAB 250Xi) with Mg Kα radiation). XPS spectra peak deconvolution and fitting were carried out using Gaussian-Lorentzian shaped peaks based on the Shirley background correction.

3 Electrochemical test and products detection

Preparation of working electrodes: Generally, disperse 5.00 mg of catalyst to 400 μL Nafion solution (volume ratio of 5% Nafion solution: absolute ethanol: deionized water=5:61:34), forming slurry A. Meanwhile, 1.00 mg conductive carbon black (to give full play to the catalytic activity of Co_2P nanodendrites, conductive carbon black was added, so as to avoid losing conductive contact with Co_2P nanodendrites far from the electrode surface) is dispersed in 100 μL Nafion solution, forming slurry B. Ultrasound slurry A and slurry B for 2 min, respectively. Then mix A and B and ultrasonic for 30 min to obtain slurry C. Take 20 μL slurry C, and drop it on the carbon paper to form the required electrode.

Electrochemical test: All electrochemical tests were performed by an H-type cell. The working electrodes (Co_2P and carbon black) and reference electrode (Ag/AgCl, saturated KCl) are located in the cathode chamber, and the counter electrode (RuIrOx@Ti foam) is located in the anode chamber. A cation exchange membrane (FAB-PK-130, Fumasep, Germany) is used to separate the cathode chamber and anode chamber, and 20 mL of 0.5 M Na_2SO_4 containing 0.1 M $NaNO_3$ solutions are filled in the cathode and anode chambers respectively. Before the electrochemical test, ultrapure Ar was bubbled into the electrolyte for more than 30 min to eliminate the influence of impurities (such as oxygen in the air). And keep Ar saturated by continuously bubbling the electrolyte with 20 sccm Ar during the test. The electrochemical workstation (CHI 660e, Shanghai CH Instruments, Co., China) is used for electrochemical data acquisition. Before the formal electrochemical test, the electrode is activated by cyclic voltammetry (CV), that is, within the potential range of -0.61~1.51 V (vs. Ag/AgCl), the electrode is scanned 40 times at the sweep speed of 100mV s^{-1}. The polarization curve (linear sweep voltammetry, LSV)) is obtained in the range of -0.61 ~ -1.51 V (vs. Ag/AgCl) with a sweep speed of 5 mV s^{-1}. In Ar-saturated 0.5 M Na_2SO_4 containing 0.1 M $NaNO_3$ catholyte, the stability of Co_2P nanodendrites was evaluated by chronoamperometry (i-t curve) at a potential of -0.6 V vs. RHE for 10 cycles (one cycle for one hour). All the potentials are referred to as the reversible hydrogen electrode (RHE) by the following conversion equation:

Neutral electrolyte: $E_{vs\ RHE} = E_{vs\ Ag/AgCl} + 0.197\ V + 0.0591 \times pH\ (V)$ (1)

Detection of ammonia product: The concentration of NH_3 in the catholyte was determined by ^1H nuclear magnetic resonance (JNM-ECZ400S, JEOL, Japan), using maleic acid ($C_4H_4O_4$) as an internal standard and DMSO-d6 as a solvent. The calibration curve of NH_4^+ is shown in Figure S3. Firstly, a series of $(NH_4)_2SO_4$ solutions with known concentrations (2, 4, 6, 8, 10, 20, 50, 100 mM) were prepared with 0.5 M Na_2SO_4 as the dispersion solution. Secondly, take 500 μL of standard $(NH_4)_2SO_4$ solutions and 100 μL of DMSO-d6 (0.2 wt.% $C_4H_4O_4$) were fully mixed, and an NMR test was carried out at room temperature. Third, obtain the peak area ratio between NH_4^+ and $C_4H_4O_4$ from the NMR results, and linearly fit the peak area ratio with the NH_4^+ concentration to obtain the calibration curve. To test the ammonia generated after NO_3^-RR, take 1.0 mL of catholyte, add 4.0 mL of 4.0 M H_2SO_4, and fully mix. Afterward, the calibration curve is made the same way. The ammonia concentration generated after NO_3^-RR can be calculated according to the peak area ratio and calibration curve. Moreover, the Faraday efficiency (FE) of ammonia can be calculated by the equation (2):

$$\text{FE（\%）} = \frac{Q_{product}}{Q_{Total}} \times 100\% = \frac{n_{product} \times N \times F}{j \times t} \times 100\%$$

(2)

Q_{product}: The quantity of electric charge needed to generate an NH_3.

Q_{total}: The total quantity of electric charge consumed.

n_{product}: The molar mass that produces an NH_3.

N: The number of electrons transferred in the reaction (the N value of NO_3^-RR is 8).

F: Faraday constant (96485 C mol^{-1}).

j: Total current density.

t: Electrolysis time.

Results and Discussion

4 Additional characterization results of the as-prepared Co_2P nanodendrites

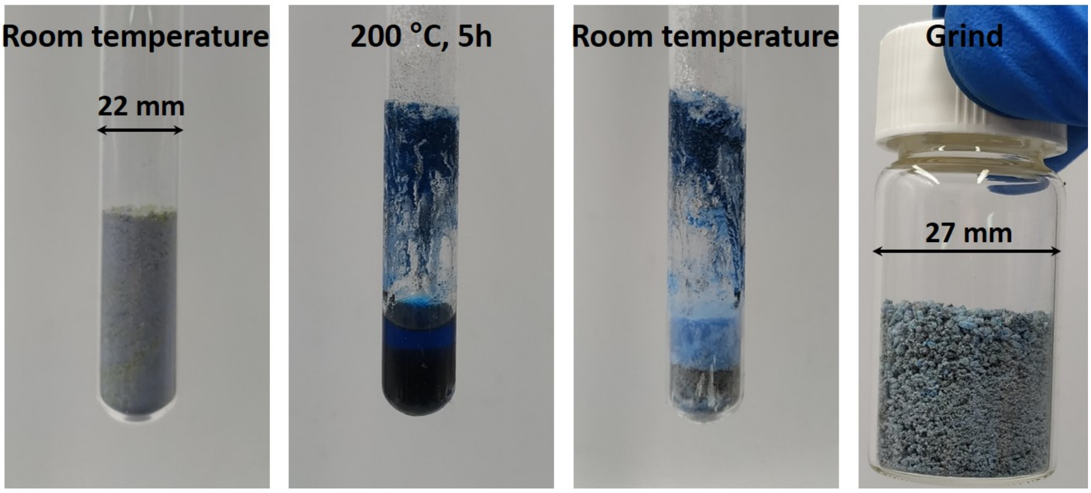

Figure S1. Digital images of reaction systems was taken before and after reaction at 200 °C for 5 h.

Table S2. NH_3 yields and FEs of Co_2P nanodendrites for the NO_3^-RR at different potentials.

Potential / V (vs. RHE)	Co_2P nanodendrites FE (%)	Yield rate (mg cm^{-2} h^{-1})
-0.2	0	0
-0.3	70.98 ± 7.66	0.46 ± 0.05
-0.4	89.91 ± 10.38	2.38 ± 0.28
-0.5	87.40 ± 7.21	3.52 ± 0.29
-0.6	88.61 ± 2.90	4.67 ± 0.15
-0.7	78.72 ± 4.51	5.58 ± 0.32
-0.8	67.05 ± 2.98	7.10 ± 0.31
-0.9	53.32 ± 3.20	9.32 ± 0.56

Table S3. NH_3 yields and FEs of Co_2P nanodendrites for the NO_3^-RR consecutive recycling test at -0.8 V vs. RHE.

Cycle number	Co_2P nanodendrites	
	FE (%)	Yield rate (mg cm^{-2} h^{-1})
1	88.13 ± 3.72	4.74 ± 0.20
2	87.85 ± 1.80	5.14 ± 0.10
3	87.27 ± 0.31	5.17 ± 0.02
4	91.02 ± 2.35	5.39 ± 0.14
5	88.01 ± 1.50	5.22 ± 0.09
6	87.84 ± 1.95	5.20 ± 0.12
7	88.95 ± 5.81	5.32 ± 0.35
8	89.76 ± 2.71	5.19 ± 0.16
9	89.31 ± 2.99	5.10 ± 0.17
10	87.60 ± 1.70	4.90 ± 0.10

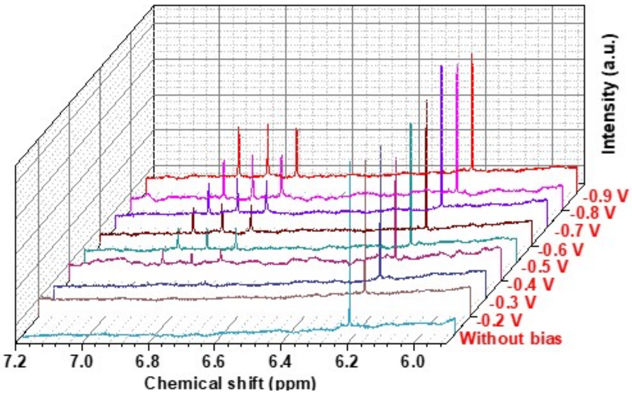

Figure S2. The ^{1}H NMR spectra of catholyte in the case of the Co_2P nanodendrites in 0.5 M Na_2SO_4 with 0.1 M $NaNO_3$ electrolyte.

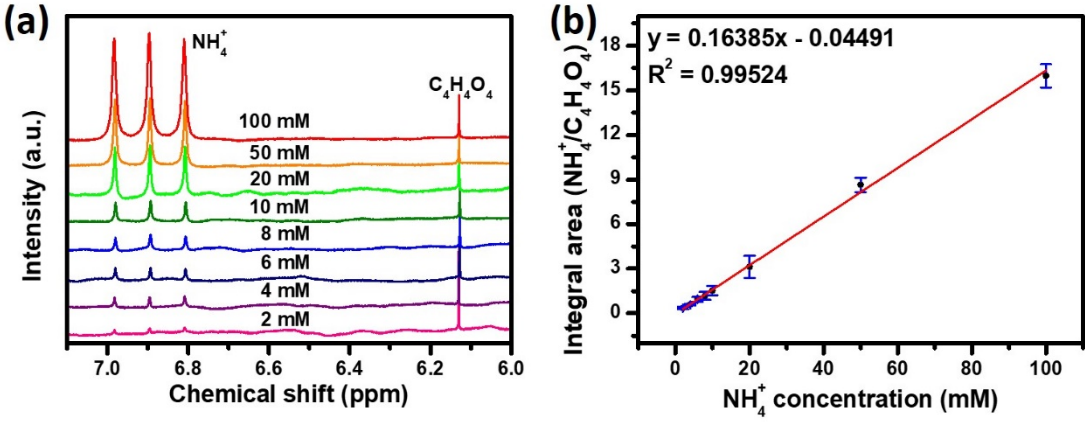

Figure S3. (a) The ^{1}H NMR spectra (600 MHz) of NH_4^+ with different concentrations. (b) The standard curve of integral area (NH_4^+ / $C_4H_4O_4$) against NH_4^+ concentration.

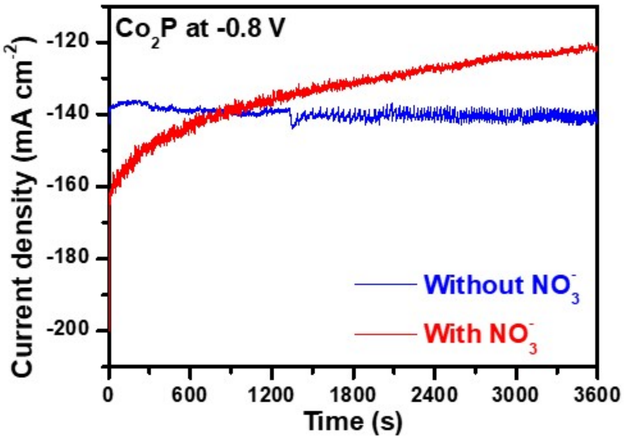

Figure S4. The chronoamperometric response of Co_2P nanodendrites in 0.5 M Na_2SO_4 with or without 0.1 M $NaNO_3$ solution at -0.8 V vs. RHE.

Note: The potential reason for the gradual decrease in current density when nitrate is present is: As electrolysis progresses, nitrate is continuously consumed, resulting in a decrease in nitrate concentration and a decrease in electrolysis current density

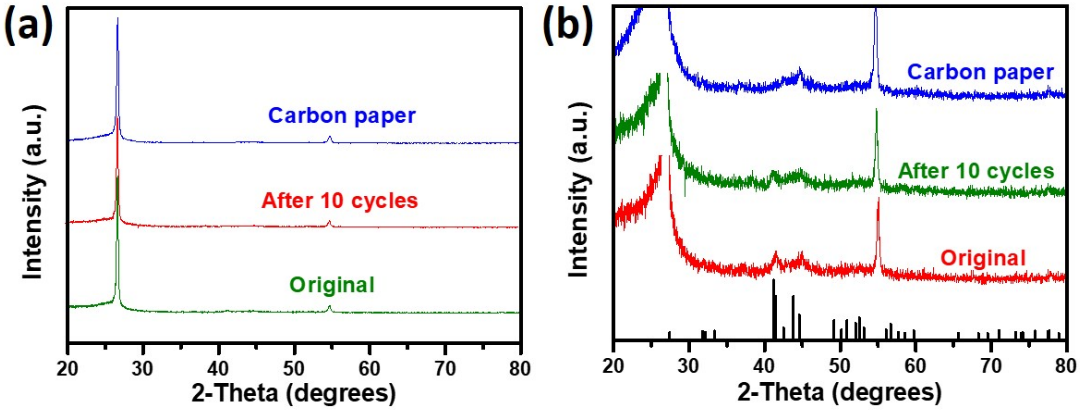

Figure S5. PXRD pattern of Co_2P nanodendrites electrode before and after ten cycles stability test.

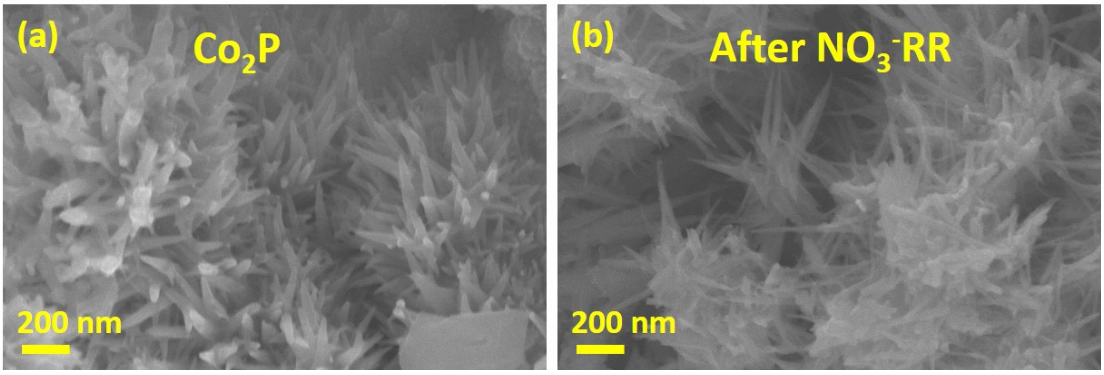

Figure S6. SEM images of Co_2P nanodendrites electrode (a) before and (b) after ten cycles of stability test.