Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

MoP supported on reduced graphene oxide for high performance electrochemical nitrogen reduction

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Experimental section

Materials:

Molybdenum (VI) dioxyacetylacetonate ($MoO_2(acac)_2$), sodium hypophosphite (NaH_2PO_2), lithium sulphate (Li_2SO_4) were purchased from Macklin Biochemical Co., Ltd., Shanghai. Ammonium chloride (NH_4Cl), trisodium citrate dihydrate ($C_6H_5Na_3O_7 \cdot 2H_2O$), ethanol ($C_2H_5OH$), hydrochloric acid (HCl) were purchased from Sinopharm Chemical Reagent Co., Ltd., Shanghai, China. Nessler's reagent, potassium sodium tartrate tetrahydrate ($C_4H_4O_6KNa \cdot 4H_2O$), p-dimethylaminobenzaldehyde ($C_9H_{11}NO$) were purchased from Aladdin Industrial Corporation. Sodium hydroxide (NaOH) was purchased from Xilong Chemical Co., Ltd. Salicylic acid ($C_7H_6O_3$), sodium nitprasside dehydrate ($Na_2[Fe(CN)_5NO] \cdot 2H_2O$), sodium hypochlorite solution (NaClO), hydrazine manahydrachlaride (ClH_5N_2) were purchased from Saen Chemical Technology Co., Ltd., Shanghai. Carbon paper was purchased from River's electric Co., Ltd., Shanghai. 5% Nafion solution, Proton exchange membrane (Nafion membrane 211) were purchased from DuPont Holding Co., Ltd., China. Distilled water (Millipore, 18.2 MΩ). All the reagents were used as received without further purification.

Characterization

XRD images were recorded using a Philips X-Pert diffractometer with Cu Kα (40 kV, 30 mA) radiation of wavelength 0.15418 nm, XPS mea were carried out on a VG ESCALAB MK II spectrometer using an Al Kα (1486.6 eV) photon source. Scanning electron microscopy (SEM) images, transmission electron microscopy (TEM), high-resolution transmission electron microscopy (HRTEM), Scanning electron microscopy (SEM) images were recorded using a Hitachi S-4800 instrument. Energy dispersive X-Ray spectroscopy (EDX) images were recorded using INCA Energy X-MAX-50 instrument. The absorbance data were measured with an ultraviolet-visible (UV-Vis) spectrophotometer (General Tu-1901).

Synthesis of MoP@rGO, MoP, rGO

75 mg $MoO_2(acac)_2$ was dissolved in 30 mL ethanol/DI mixed solvent (V/V=1) under strong agitation. 50 mg GO was then added into the above solution .Ultrasound was then continued for 30 min to form a uniform suspension. The uniform suspension was dried with stirring at temperature of 80 ℃. The obtained precursor powder was grounded and transferred into a tube furnace near the Ar outlet, and NaH_2PO_2 (1.0 g) were placed near the Ar inlet. The sample was calcined at 500 ℃ for 1 h and then calcined at 750 ℃ for another 2 h. The heating rate of the two heating processes were 2 ℃ min^{-1} and 5 ℃ min^{-1}. Ar gas was continuously injected during calcination. The sample was washed several times with deionized water, and then dried under ambient condition. For comparison, MoP was prepared in the same process without GO. rGO was prepared in the same process without MoP.

Electrochemical NRR measurements:

The electrochemical experiments were performed on the CHI 660E electrochemical workstation with the standard three electrode system. MoP@rGO, MoP, rGO were drop-casted on CP (1 cm × 1 cm × 2 sides,) and applied as the working electrode, graphite rod as counter electrode and the saturated Ag/AgCl electrode as the reference electrode. All potentials were converted to RHE with the following equation: $E_{RHE} = E_{Ag/AgCl} + 0.197 + 0.059pH$. Before electrochemical NRR measurements, the electrolyte (30 mL) was purged with 99.99% N_2 or Ar for 30 min. Potentiostatic tests were conducted in N_2 or Ar saturated electrolyte in the two compartment cell, which was separated by proton exchange membrane (Nafion membrane 211). During the process of potentiostatic tests, 99.99% N_2 or Ar were continuously fed into the cathodic chamber.

Prepartion MoP@rGO/CP, MoP/CP, rGO/CP

2.5 mg MoP@rGO and 50 μL Nafion solution (5 wt%) were dispersed in 450 μL ethanol with sonication for 30 min to form a homogeneous ink. Then 200 μL of MoP@rGO ink was loaded on a carbon paper electrode with area of 1 cm^2 and dried under ambient condition. MoP/CP, rGO/CP was made by the same process.

Determination of NH_3

The concentration of the produced NH_3 during NRR was determined by the indophenol blue method.[1] Typically, 1mg mL^{-1} NH_4^+ solution was prepared and diluted to 1 µg mL^{-1}. Standard NH_4^+ solution with NH_4^+ concentrations of 0.0, 0.1, 0.2, 0.4, 0.6, 0.8 and 1.0 µg mL^{-1} were prepared in 10 mL colorimetric tubes by diluted 0.1 M Li_2SO_4 (pH = 3) . Then 500 µL of 1.0 M NaOH solution containing sodium citrate (5.0 wt%) and salicylic (5.0 wt%) was added to the above 10 mL of sample solution. Subsequently, 100 µL of sodium nitroferricyanide solution (1.0 wt%) and 100 µL of NaClO solution (0.55 M) were added to the above mixture. After standing at room temperature for 1 h, the UV–vis absorption spectrum was measured at a wave length of 690 nm. After potentiostatic tests,10 mL electrolyte was obtained from cathodic chamber and developed color by indophenol blue method. The fitting curve ($y = 0.74x+0.035$, $R^2 = 0.999$) showed good linear relation between the NH_4^+ concentration and absorbance values

Determination of N_2H_4:

The Watt and Chrisp method was applied to analyze the N_2H_4 yield in the electrolyte.[2] Typically, 2 mg mL^{-1} N_2H_4 solution was firstly diluted to 2 µg mL^{-1}. Standard N_2H_4 solution with N_2H_4 concentrations of 0.2, 0.6, 1.2, 1.5 and 2.0 µg mL^{-1} were prepared in 10 mL colorimetric tubes in 0.1 M Li_2SO_4 (pH = 3) .The p-$C_9H_{11}NO$ (5.99 g), HCl (30 mL), and C_2H_5OH (300 mL) were mixed as a color reagent. In detail, 5.0 mL standard N_2H_4 solution was removed and 5.0 mL of color reagent then added with rapid stirring for several times at room temperature. After incubation for 20 min, the mixture was measured on an UV–Vis Tu-1901 spectrophotometer with absorbance at the wavelength of 460 nm. The fitting curve ($0.747x+0.007$, $R^2 = 0.999$) showed good linear relation between the N_2H_4 concentration and absorbance values.

Calculations of NH_3 yield and faradaic efficiency:

The rate of NH_3 yield was calculated using the following equation:

NH_3 yield rate = $(C_{NH4}{}^{+} \times V)/(t \times m_{cat})$,

To calculate the Faradaic efficiency (FE), the following equation was applied:

FE = $3F \times C_{NH4}{}^{+} \times V/(18 \times Q)$,

where $C_{NH4}{}^{+}$ is the measured NH_4^+ concentration, V is the total volume of electrolyte, t is the duration of applied potential, m_{cat} is the mass of catalyst loaded on the working electrode, F is the Faradaic constant, and Q is the quantity of applied electricity.

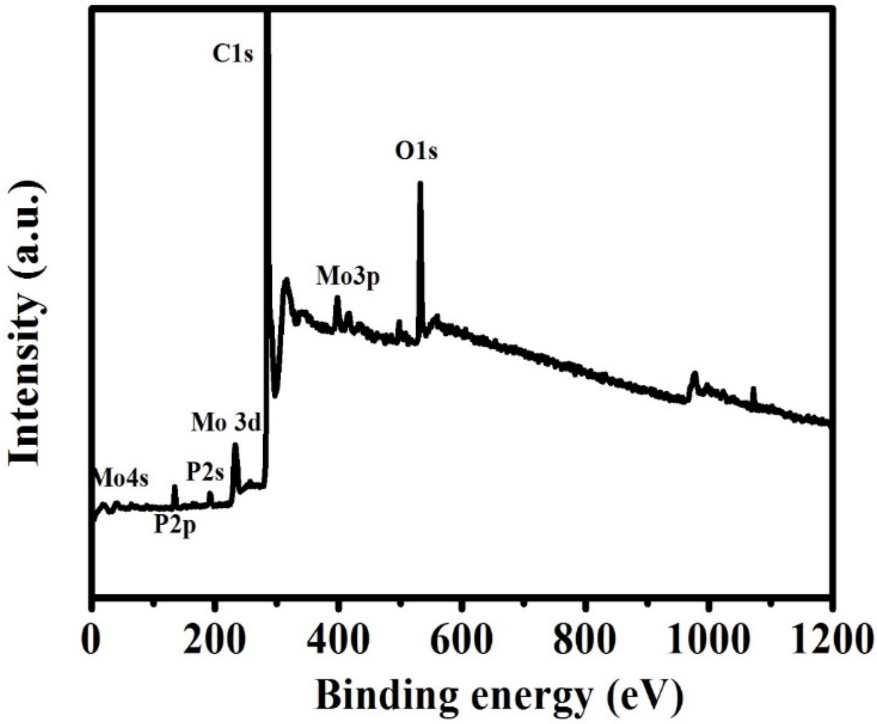

Figure S1 Full survey of XPS spectrum of MoP@rGO.

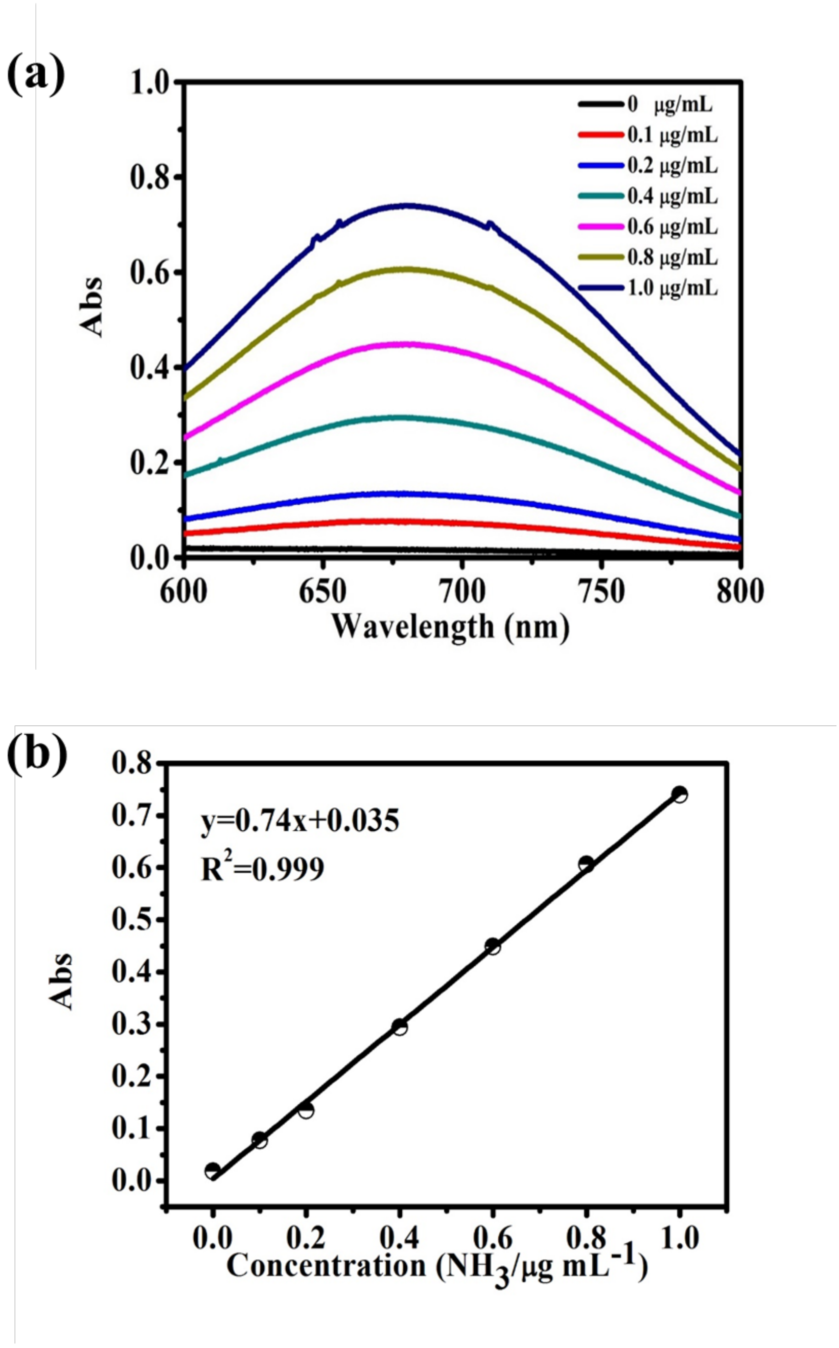

Figure S2 (a) UV-Vis spectra of indophenol assays kept with different concentration of NH_4^+ ions for 1 h at room temperature. (b) A calibration curve used to estimate the concentrations of NH_4^+ ions.

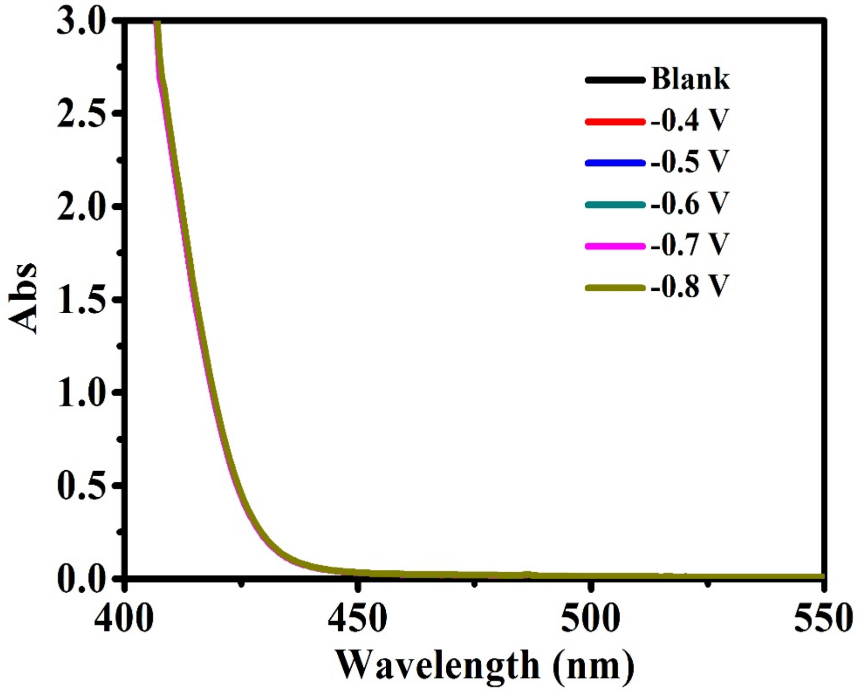

Figure S3 UV-Vis absorption spectrum of MoP@rGO electrolysis in N_2-saturated solution at -0.6 V *vs*. RHE for 2 h after incubated with N_2H_4 color agent for 20 min at room temperature.

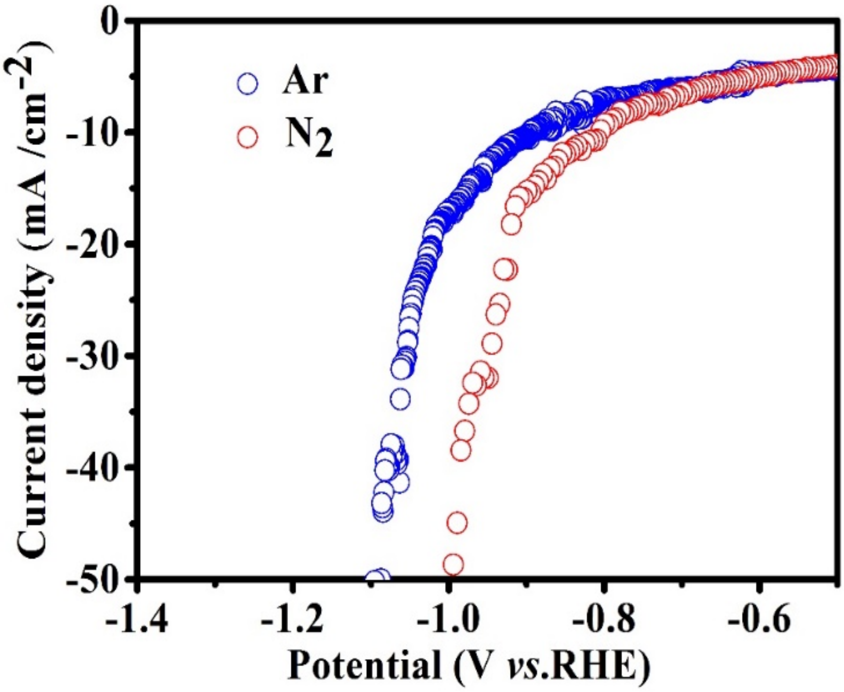

Figure S4 LSV curves of MoP@rGO in N2- (red line) and Ar-saturated (blue line) electrolyte.

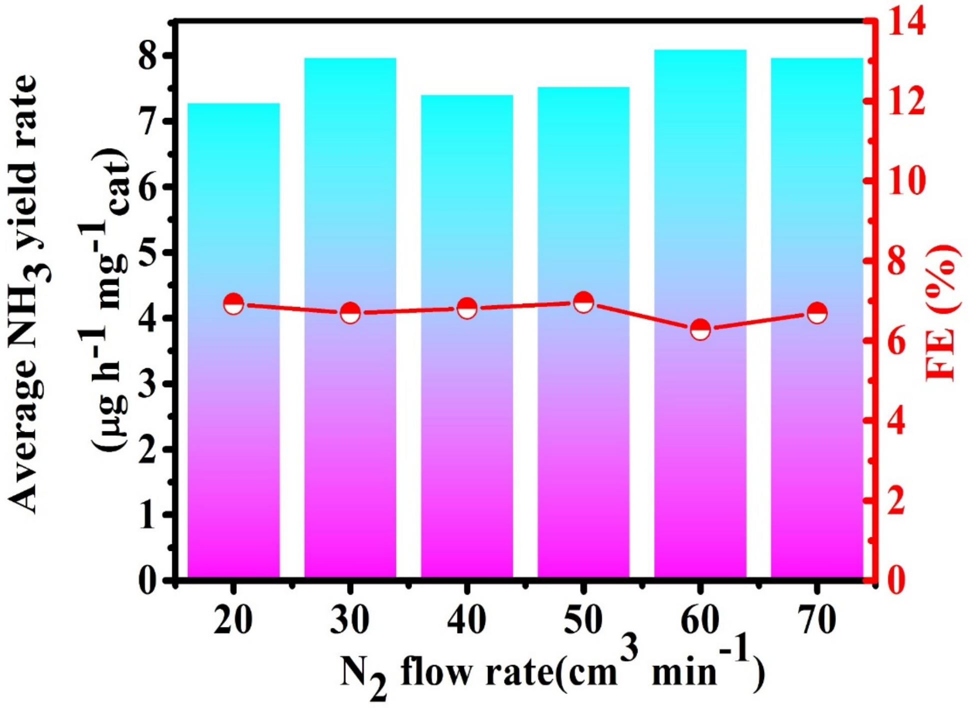

Figure S5 NH_3 synthesis yield rate and corresponding Faradaic efficiency at -0.6 V *vs*. RHE on MoP@rGO electrode at different N_2 flow rate (20 to 70 cm^3 min^{-1}).

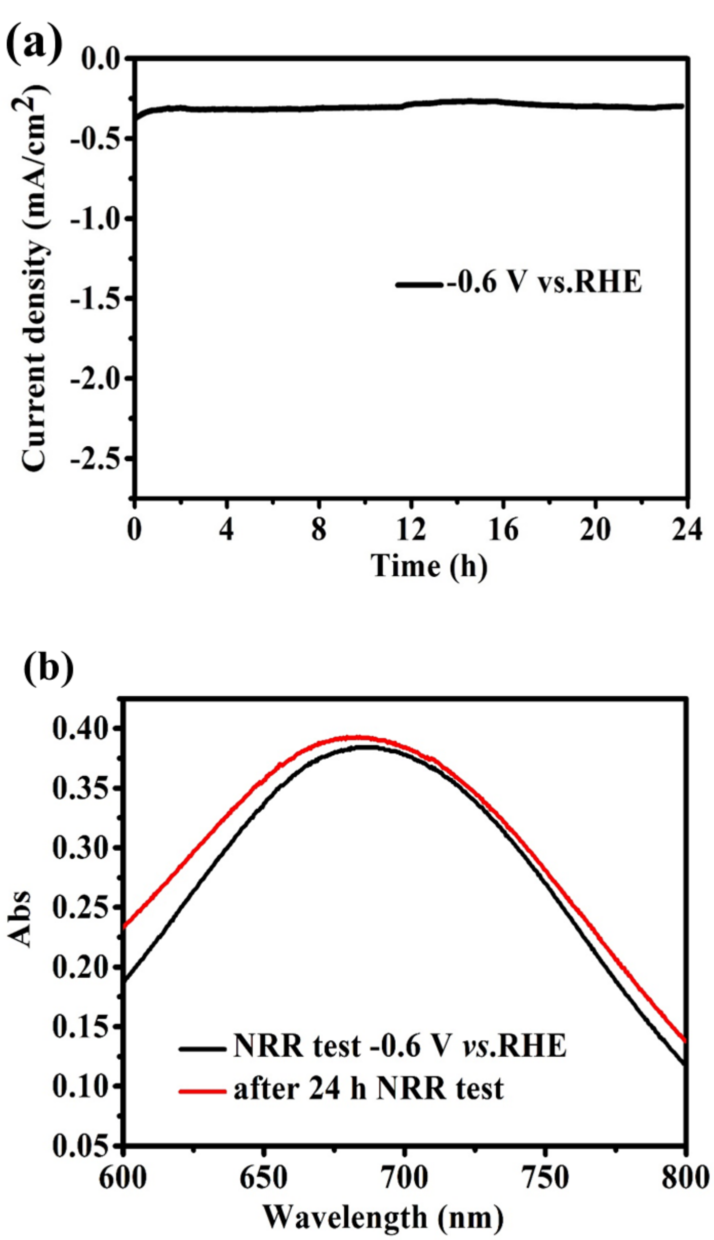

Figure S6 (a) Chronoamperometry curve of NRR test of MoP@rGO. (b) UV-vis absorption spectra of electrolytes obtained with indophenol indicator (Color code: blank line: electrolysis in N_2-saturated solution at -0.6 V *vs*. RHE for 2 h at MoP@rGO electrode, red line: electrolysis in N_2-saturated solution at -0.6 V *vs*. RHE for 2 h on MoP@rGO electrode after 24 h continuous NRR test.

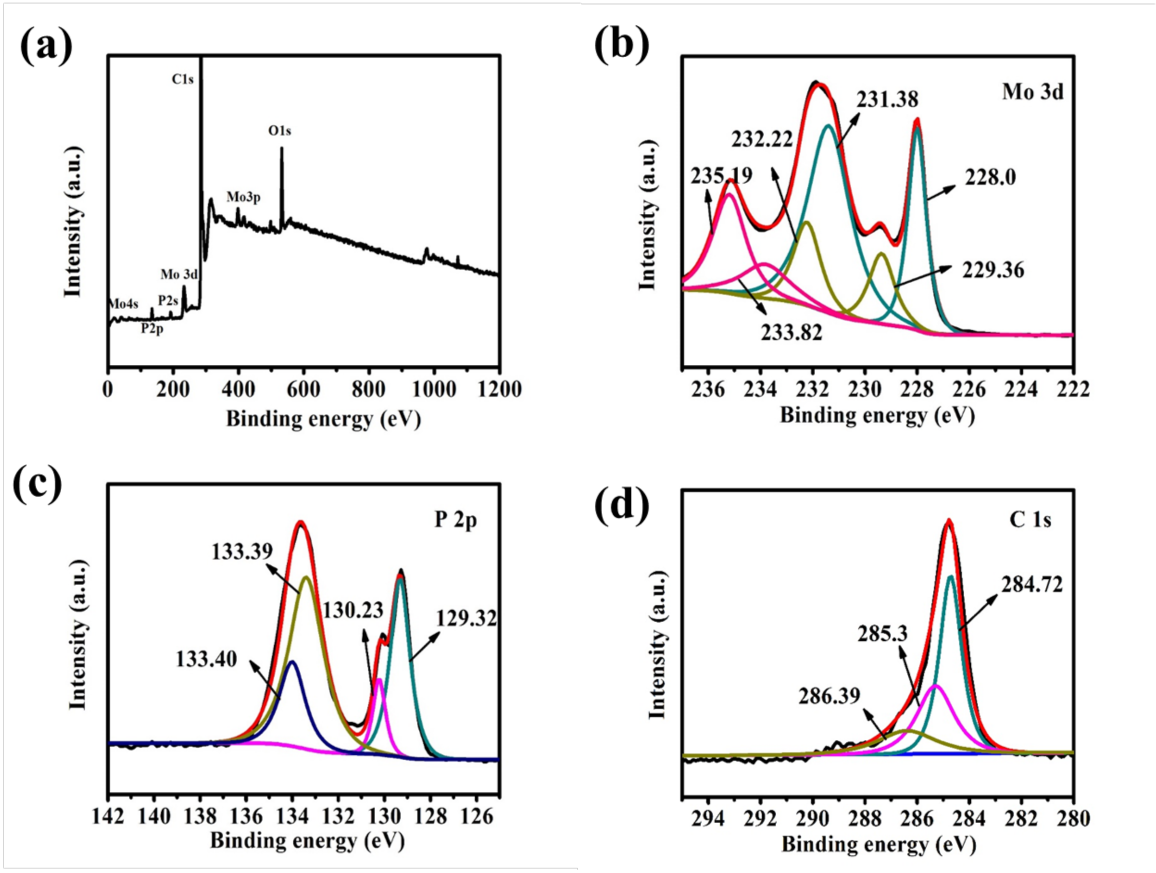

Figure S7 XPS spectra of MoP@rGO hybrids after NRR tests: (a) XPS survey spectrum for MoP@RGO, (b) Mo 3d , (c) P 2p , (d) C1s.

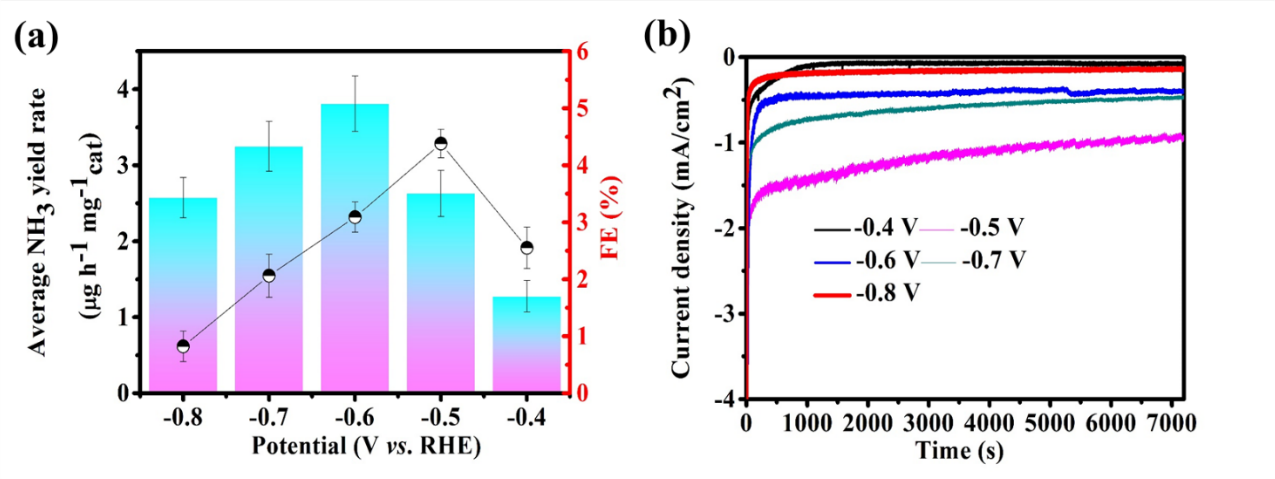

Figure S8 Catalytic performances of MoP in 0.1 M Li_2SO_4 aqueous solution (pH=3). (a) NH_3 synthesis yield rate and corresponding Faradaic efficiency of MoP. (b) Chronoamperometry curves of continues N_2 reduction on MoP electrode.

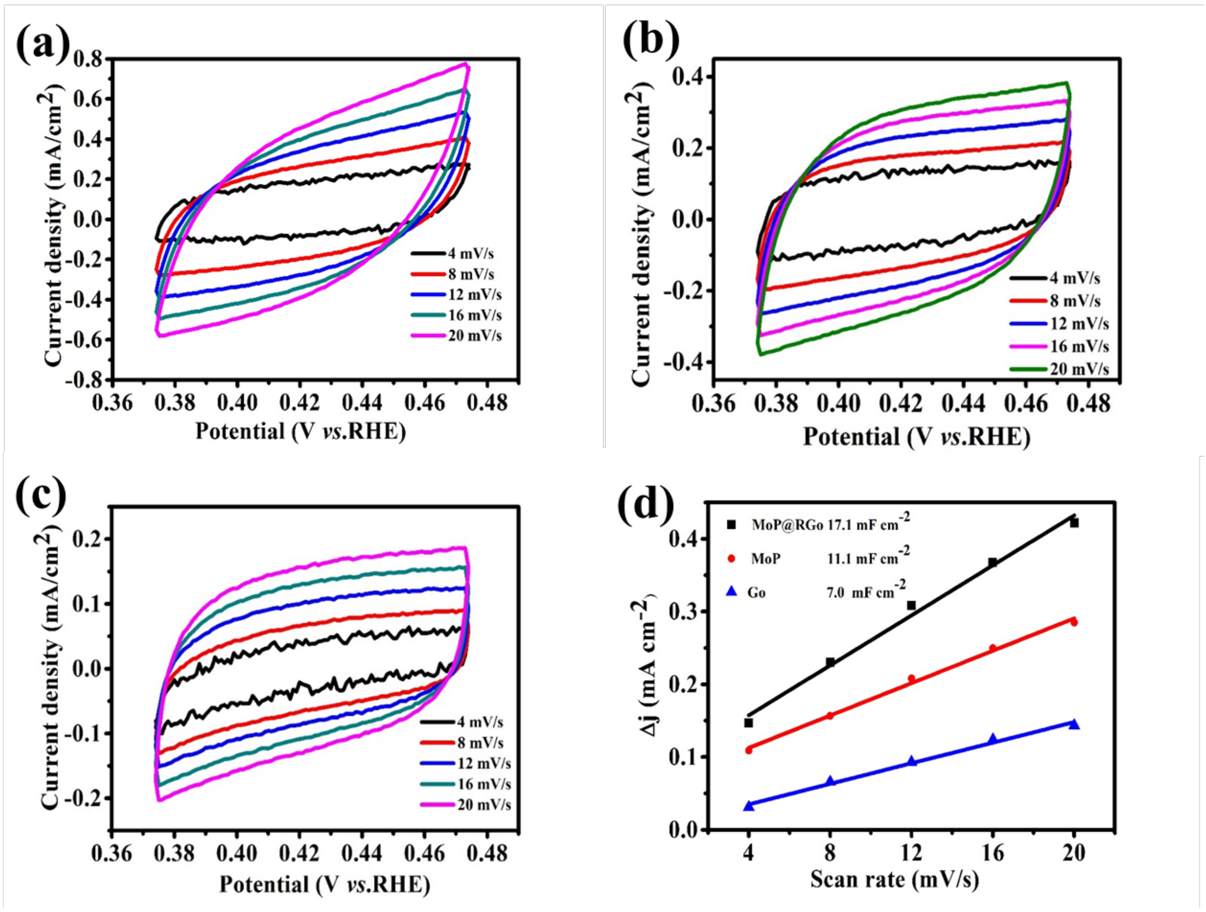

Figure S9 Cyclic voltammograms of (a) MoP@rGO, (b) MoP and (c) rGO at various scan rates (4 to 20 mV s^{-1}) in the regions of 0.38 to 0.48 V *vs*. RHE. (d) The capacitive current densities at various scan rates (4 to 20 mV s^{-1}) for MoP@ rGO, MoP and rGO.

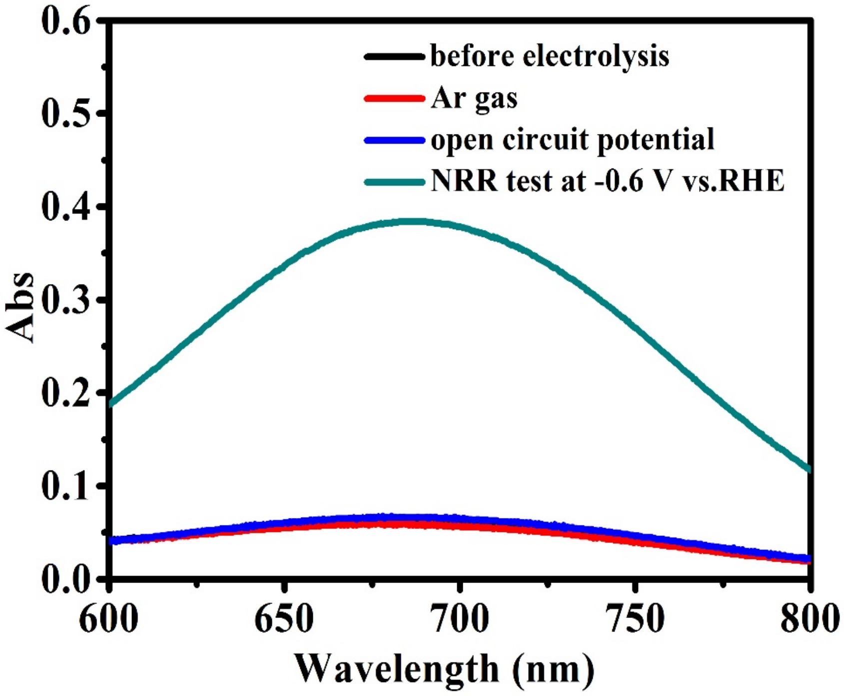

Figure S10 UV-Vis spectra of electrolytes after colored with indophenol indicator after 2 h NRR tests under different condition. (Color code: blank line, 0.1 M Li_2SO_4 aqueous solution before electrolysis; red line, electrolysis in Ar-saturated at -0.6 V *vs*. RHE for 2 h; blue line, electrolysis in N_2-saturated solution at open circuit potential for 2 h. green line NRR test at -0.6 V vs. RHE .

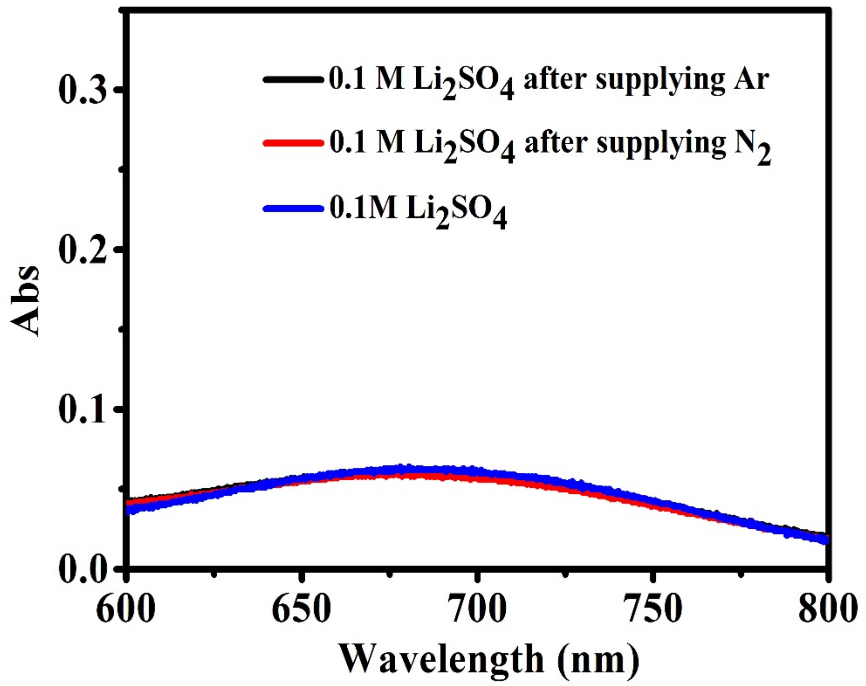

Figure S11 UV-Vis spectra of electrolytes after colored with indophenol indicator under different condition.(Color code: blank line, 0.1 M Li_2SO_4 aqueous solution after supplying Ar for 30 min; red line 0.1 M Li_2SO_4 aqueous solution after supplying N_2 for 30 min; blue line: 0.1 M Li_2SO_4 aqueous solution without any pretreatment.

References

1. Y. Liu, M. Han, Q. Xiong, S. Zhang, C. Zhao, W. Gong, G. Wang, H. Zhang and H. Zhao, *Advanced Energy Materials*, 2019, **9**, 1803935.
2. S. Kang, J. Wang, S. Zhang, C. Zhao, G. Wang, W. Cai and H. Zhang, *Electrochemistry Communications*, 2019, **100**, 90-95.