### Supporting Information

### Support Effect Boosting Electrocatalytic N<sub>2</sub> Reduction Activity of Ni<sub>2</sub>P/N,P-Codoped Carbon NanoSheet Hybrids

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**Figure S1.** (a) XRD patterns of  $Ni_2P$ ; (b) SEM images of  $Ni_2P$  and (c-d) the corresponding elemental mapping.

Figure S2. Liner sweep voltammetry (LSV) of bulk Ni<sub>2</sub>P.

**Table S1.** Comparison of HER activity of as-prepared bulk  $Ni_2P$  with previously reported  $Ni_2P$ based materials in acidic solution.

**Figure S3.** Calculation model of Ni<sub>2</sub>P alloy supported on one-layer N-doped graphene (Ni<sub>2</sub>P/N-C). Gray, blue, green and pink balls represent the C, N, Ni and P atoms.

**Figure S4.** Calculation model of Ni<sub>2</sub>P alloy supported on one-layer graphene with N and P-doped (Ni<sub>2</sub>P/N,P-C). Gray, blue, green and pink balls represent the C, N, Ni and P atoms.

**Figure S5.** FESEM images of melamine-phytic acid-nickel acetate (Me-PA-Ni) compounds in low (a) and high (b,c) resolution.

**Figure S6.** (a) FTIR spectra of melamine (Me), phytic acid (PA) and Me-PA-Ni; (b) the structure of Me-PA-Ni, and the blue dotted line represents a structural unit.

Figure S7. XPS spectra of the as-fabricated Me-PA-Ni: (a) survey spectrum and (b) P 2p photoelectron.

Figure S8. XRD patterns of N,P-C.

**Figure S9.** N<sub>2</sub> adsorption/desorption isotherm of (a) Ni<sub>2</sub>P/N,P-C, (b) N,P-C and the corresponding pore size distribution of (c) Ni<sub>2</sub>P/N,P-C, (d) N,P-C.

**Figure S10.** The well-resolved lattice fringe of Ni<sub>2</sub>P/N,P-C in Fig. 2h were calculated based on Nano Measurer software analysis.

Figure S11. EDX spectrum of the as-fabricated Ni<sub>2</sub>P/N,P-C.

**Figure S12.** (a) XRD pattern of the residue of  $Ni_2P/N,P-C$  after TGA measurement and (b) the corresponding TGA curve of  $Ni_2P/N,P-C$  in air atmosphere.

Figure S13. Raman spectra of Ni<sub>2</sub>P/N,P-C and N,P-C.

Figure S14. XPS spectra of C 1s for bulk Ni<sub>2</sub>P.

Figure S15. XPS spectra of C 1s for Ni<sub>2</sub>P/N,P-C.

Figure S16. XPS spectra of (a) N 1s for Ni<sub>2</sub>P/N,P-C and (b) Ni 2p for Ni<sub>2</sub>P/N,P-C and Ni<sub>2</sub>P/N-C.

Figure S17. Optical photograph of the three-electrode device for N<sub>2</sub>RR testing.

Scheme S1. N<sub>2</sub>RR experimental procedures we utilized in this article.

**Figure S18.** Cyclic voltammetry (CV) curves of  $Ni_2P/N_PC$  in both Ar-saturated (black line) and  $N_2$ -saturated (red line) 0.1 M HCl electrolyte at 50 mV s<sup>-1</sup>.

**Figure S19.** (a) UV-vis curves and (b) concentration-absorbance of NH<sub>4</sub>Cl solution with a series of standard concentration. The absorbance at 655 nm was measured by UV-vis spectrophotometer. The standard curve showed good linear relation of absorbance with NH<sub>4</sub>Cl concentration (y=0.1376x+0.0285, R<sup>2</sup>=0.9999); (c) UV-vis curves and (d) concentration-absorbance of NH<sub>4</sub>Cl solution with a series of standard concentration (0-2 µg mL<sup>-1</sup>) in 0.1 M HCl. The absorbance at 655 nm was measured by UV-vis spectrophotometer. The standard curve showed good linear relation of absorbance with NH<sub>4</sub>Cl concentration (y=0.1376x+0.0286, R<sup>2</sup>=0.9998); (e) UV-vis curves and (f) concentration-absorbance of NH<sub>4</sub>Cl solution with a series of standard concentration (y=0.1376x+0.0286, R<sup>2</sup>=0.9998); (e) UV-vis curves and (f) concentration-absorbance of NH<sub>4</sub>Cl solution with a series of standard concentration ( $0-2 \ \mu g \ mL^{-1}$ ) in 0.2 M PBS. The absorbance at 655 nm was measured by UV-vis spectrophotometer. The standard curve showed good linear relation of absorbance with NH<sub>4</sub>Cl concentration-absorbance at 655 nm was measured by UV-vis spectrophotometer. The standard curve showed good linear relation of absorbance with NH<sub>4</sub>Cl concentration (y=0.1356x+0.0486, R<sup>2</sup>=0.9987); (g) UV-vis curves and (h) concentration-absorbance of NH<sub>4</sub>Cl solution with a series of standard curve showed good linear relation (y=0.10356x+0.0486, R<sup>2</sup>=0.9987); (g) UV-vis curves and (h) concentration-absorbance of NH<sub>4</sub>Cl solution with a series of standard curve showed good linear relation (y=0.1035x+0.0395, R<sup>2</sup>=0.9981).

**Figure S20.** (a) UV-vis curves and (b) concentration-absorbance of  $N_2H_4$  solution with a series of standard concentration. The absorbance at 455 nm was measured by UV-vis spectrophotometer. The standard curve showed good linear relation of absorbance with  $N_2H_4$  concentration (y=1.1158x+0.0252, R<sup>2</sup>=0.9999).

**Figure S21.** (a) UV-Vis spectra of electrolytes colored with indophenol indicator after 2h electrocatalytic reduction at different potentials; (b) Gas chromatography (GC) data of the amounts of  $H_2$  from the headspace of the cell for  $N_2RR$  on the  $Ni_2P/N_1P-C$  catalyst in  $N_2$ -saturated 0.1 M HCl at various potentials; (c) The calculated FE of HER; (d) NH<sub>3</sub> yield rate and Faradaic

efficiency (blue line) of  $Ni_2P/N,P-C$  in different electrolyte at -0.2 V; (e) reaction kinetic studies of  $Ni_2P/N,P-C$ ,  $Ni_2P$  and N,P-C; (f-h) reaction kinetic studies of  $Ni_2P/N,P-C$  in different electrolyte.

**Figure S22.** (a) UV-vis absorption spectra of the 0.1 M HCl electrolyte (after charging at different potentials for 2h) after incubated for 15 min at room temperature; nitrogen temperature-programmed desorption (N<sub>2</sub>-TPD) spectra of (b) Ni<sub>2</sub>P and (c) Ni<sub>2</sub>P/N,P-C.

**Figure S23.** (a) The FE and NH<sub>3</sub> yield rate of Ni<sub>2</sub>P/N,P-C physically mixed Ni<sub>2</sub>P and N,P-C; (b) SEM images of Ni<sub>2</sub>P/P-C and the corresponding elemental mapping; (c) SEM images of Ni<sub>2</sub>P/N-C and the corresponding elemental mapping; (d) The FE of Ni<sub>2</sub>P/P-C and Ni<sub>2</sub>P/N-C; Difference charge densities of (e) Ni<sub>2</sub>P alloy supported on one-layer graphene with P-doped, where the isosurface value is set to be 0.003 e/Å<sup>3</sup> and the positive and negative charges are showed in yellow and cyan, respectively. Gray, green and pink balls represent the C, Ni and P atoms, respectively; (f) Planar-averaged electron density difference  $\Delta \rho(z)$  for (e) Ni<sub>2</sub>P alloy supported on one-layer graphene with P-doped. Inset is the 3D isosurface of the electron density difference, the gray areas represent Ni<sub>2</sub>P alloy of the electron density difference.

**Figure S24.** CV curves of (a) Ni<sub>2</sub>P/N,P-C; (b) Ni<sub>2</sub>P with different scan rates from 20 to 140 mV/s;  $\Delta J$  of catalysts plotted against scan rate at the potential of -0.1 V vs. RHE of (c) Ni<sub>2</sub>P/N,P-C and (d) Ni<sub>2</sub>P.

Figure S25. Nyquist plots of electrochemical impedance spectra (EIS) of Ni<sub>2</sub>P/N<sub>3</sub>P-C and Ni<sub>2</sub>P.

**Figure S26.** (a) UV-vis spectra of the electrolyte stained with indophenol indicator for the work electrode in N<sub>2</sub>-saturated solution, without and after 2h electrolysis at the potential of -0.2 V in Arsaturated solution, without electrolysis in N<sub>2</sub>-saturated solution; Example data sets used to demonstrate calculation of Faradaic efficiency with and without background Ar measurements. (b) and (c) represent the NH<sub>3</sub> yield rate and FE of Ni<sub>2</sub>P/N,P-C tested in Ar- or N<sub>2</sub>-bubbled electrolyte (0.1 M HCl) with no electro-chemistry (represent by Ar and N<sub>2</sub>, respectively) and then Ar- or N<sub>2</sub>-bubbled electrolyte under applied potential (represent by Ar+Echem and N<sub>2</sub>+Echem, respectively).

**Figure S27.** (a) <sup>1</sup>H NMR spectra (700 MHz) for <sup>15</sup>N<sub>2</sub>, N<sub>2</sub> and Ar were fed to the cell in the absence of polarization; (b) <sup>1</sup>H NMR spectra (700 MHz) for <sup>14</sup>NH<sub>4</sub><sup>+</sup> and <sup>15</sup>NH<sub>4</sub><sup>+</sup> produced from N<sub>2</sub> electrochemical reduction using N<sub>2</sub> and <sup>15</sup>N<sub>2</sub> as the feeding gas, respectively; (c) <sup>1</sup>H NMR spectra (700 MHz) of various <sup>15</sup>NH<sub>4</sub>Cl concentration; (d) Integral area (<sup>15</sup>NH<sub>4</sub><sup>+</sup> / C<sub>4</sub>H<sub>4</sub>O<sub>4</sub>) against various <sup>15</sup>NH<sub>4</sub>Cl concentration; (e) <sup>1</sup>H NMR spectra (700 MHz) of the electrolyte that reacted on Ni<sub>2</sub>P/N,P-C at -0.2 V for 2h under <sup>15</sup>N<sub>2</sub> conditions; (f) The <sup>15</sup>NH<sub>4</sub><sup>+</sup> concentration of the electrolyte that was quantitatively determined by <sup>1</sup>H NMR with external standards; (g) UV-vis curves and (h) concentration-absorbance of NH<sub>4</sub>Cl solution with a series of standard concentration (0-10 µg mL<sup>-1</sup>) in 0.1 M HCl determined by Nessler's reagent method. The absorbance at 420 nm was measured by UV-vis spectrophotometer. The standard curve showed good linear relation of absorbance with NH<sub>4</sub>Cl concentration (y=0.0501x+0.0450, R<sup>2</sup>=0.9991).

**Figure S28.** (a) UV-Vis spectra of electrolytes colored with Nessler's reagent after 2h electrocatalytic reduction at -0.2V; (b) The chronoamperometric curves of  $Ni_2P/N_3P-C$  in  $N_2$ -saturated 0.1 M HCl electrolyte at various potentials for 24h.

**Figure S29.** FESEM images of Ni<sub>2</sub>P/N,P-C in low (a) and high (b) resolution after electrolysis for 2h at -0.2 V vs. RHE.

**Figure S30.** XPS spectra of (a) Ni 2p and (b) P 2p for Ni<sub>2</sub>P/N,P-C after electrolysis for 2h at -0.2 V vs. RHE.

Figure S31. XRD patterns of Ni<sub>2</sub>P/N,P-C after electrolysis for 2h at -0.2 V vs. RHE.

Figure S32. The fully optimized structure of (a)  $Ni_2P(111) / N_2P$  and (b)  $Ni_2P(111)$ .

**Figure S33.** (a) The front view and (b) side view of optimized structure of  $N_2$  adsorption on the  $Ni_2P$  (111) / N,P-C surface for the end-on and (c) the front view and (d) side view for side-on configurations. Gray, blue, green and pink balls represent the C, N, Ni and P atoms, respectively.

Figure S34. (a) The front view and (b) side view of optimized structure of N<sub>2</sub> adsorption on the P

site of  $Ni_2P(111) / N_PC$  surface via the end-on configurations. Gray, blue, green and pink balls represent the C, N, Ni and P atoms, respectively.

**Figure S35.** (a) The front view and (b) side view of optimized structure of  $N_2$  adsorption on Ni<sub>2</sub>P (111) / N,P-C surface via the end-on configurations and the corresponding difference charge density from (c) the front view and (d) side view. The isosurface value is set to be 0.001 e/Å<sup>3</sup> and the positive and negative charges are showed in yellow and cyan, respectively. Gray, blue, green and pink balls represent the C, N, Ni and P atoms, respectively; (e-k) The models of different intermediates adsorbed on the Ni<sub>2</sub>P/N,P-C based on alternating mechanisms and the corresponding charge distribution based on Difference charge density analysis.

**Figure S36.** Optimized structure of (a) H adsorption and (b)  $N_2$  adsorption on the Ni<sub>2</sub>P (111) surface, and the corresponding (c) Free energy diagrams for H and N<sub>2</sub> adsorption; Optimized structure of (d) H adsorption and (e)  $N_2$  adsorption on the Ni<sub>2</sub>P (111) / N,P-C surface, and the corresponding (f) Free energy diagrams for H and N<sub>2</sub> adsorption. Gray, blue, green, white and pink balls represent the C, N, Ni, H and P atoms, respectively.

Figure S37. Free energy diagrams for N<sub>2</sub> and N<sub>2</sub>H adsorbed on Ni<sub>2</sub>P and Ni<sub>2</sub>P/N,P-C.

**Table S2.** Comparison of the electrocatalytic activity of  $Ni_2P/N_1P-C$  to produce  $NH_3$  through  $N_2RR$  with previously reported  $N_2RR$  electrocatalysts.

Table S3. Electrochemical tests and controls to rigorously evaluate the N<sub>2</sub>RR activity.

Figure S1. (a) XRD patterns of  $Ni_2P$ ; (b) SEM images of  $Ni_2P$  and (c-d) the corresponding elemental mapping.

In **Figure S1a**, the peaks at 40.7°, 44.6°, 47.4°, 54.2°, 55.0°, 66.4°, 72.7°, 74.8°, 80.2° and 88.8° correspond to (111), (201), (210), (300), (211), (310), (311), (400), (302) and (321) planes of Ni<sub>2</sub>P (JCPDS: 89-2742, hexagonal phase, P-62m, a cell size of  $5.859 \times 5.859 \times 3.382$  nm). This result demonstrates that we successfully synthesized bulk Ni<sub>2</sub>P. However, as revealed by scanning electron microscopy (SEM) image, as-prepared Ni<sub>2</sub>P suffers from serious aggregation (**Figure S1b**). And the corresponding elemental mapping (**Figure S1c-d**) show the uniform distribution of Ni and P element.



Figure S2. Liner sweep voltammetry (LSV) of bulk Ni<sub>2</sub>P.

**Table S1.** Comparison of HER activity of as-prepared bulk  $Ni_2P$  with previously reported  $Ni_2P$ -based materials in acidic solution.

Catalysts	Mass loadin g (mg/c m <sup>2</sup> )	Electrol yte	Overpote ntial at 10 mA cm <sup>-</sup> <sup>2</sup> (mV vs. RHE)	Reference
Bulk Ni <sub>2</sub> P	0.3	0.1 M HCl	237	This work
С е О	0.254	0.5 H <sub>2</sub> SO <sub>4</sub>	185	Int J Hydrogen Energ, 2018, 43, 3697-3704

X /C 0S C e 0 X /C oS Ni<sub>2</sub>P nanobelts



### P

0	
2	

### 0 r e

### S h e

### a n

### 0 p a r

# t i **C**

### e S

### 

# 

### e S h



### a n 0 p

# a r t

С				
e				
S				
Ni <sub>2</sub> P NPs@NPC				
Unsupporte	0.429	0.5	295	ChemelectroChem,

d Ni <sub>2</sub> P	H <sub>2</sub> SO <sub>4</sub>		10.1002/celc.201600543
Nano-sized Ni <sub>2</sub> P	 0.5 H <sub>2</sub> SO <sub>4</sub>	170	J.Catal.,2015, 326, 92-99



**Figure S3.** Calculation model of Ni<sub>2</sub>P alloy supported on one-layer N-doped graphene (Ni<sub>2</sub>P/N-C). Gray, blue, green and pink balls represent the C, N, Ni and P atoms.



**Figure S4.** Calculation model of Ni<sub>2</sub>P alloy supported on one-layer graphene with N and P-doped (Ni<sub>2</sub>P/N,P-C). Gray, blue, green and pink balls represent the C, N, Ni and P atoms.

**Figure S5.** FESEM images of melamine-phytic acid-nickel acetate (Me-PA-Ni) compounds in low (a) and high (b) resolution.



**Figure S6.** (a) FTIR spectra of melamine (Me), phytic acid (PA) and Me-PA-Ni; (b) the structure of Me-PA-Ni, and the blue dotted line represents a structural unit.

As shown in **Figure S6a**, the characteristic band appears at  $\approx 813$  cm<sup>-1</sup> can be assigned to the triazine ring vibration of Me and shifts to 783 cm<sup>-1</sup> in Me-PA-Ni, which confirms that he deformation of the aromatic ring and protonation of the triazine rings in Me-PA-Ni. The band appear at 957 and 1127 cm<sup>-1</sup> correspond to PO<sub>4</sub><sup>3-</sup> groups in PA and shift to 1072 and 1173 cm<sup>-1</sup> in Me-PA-Ni, a token of the hydrogen bonding between Me and PA. Based on these results, we

verify that the formation of -Me-(Ni-phytate)-Me- structure assembled by hydrogen bonding and self-assembles into the 2D networks<sup>[1]</sup> as shown in **Figure S6b**.

Figure S7. XPS spectra of the as-fabricated Me-PA-Ni: (a) survey spectrum and (b) P 2p photoelectron.

As displayed in **Figure S7a**, the full survey XPS spectrum of  $Ni_2P/N,P-C$  verifies that the presence of Ni, P, N, O and C. In P 2p region (**Figure S7b**), the main peak locate at 133.5 eV, confirming the formation of metal-phytate<sup>[2,3]</sup>.



Figure S8. XRD patterns of N,P-C.
**Figure S9.** N<sub>2</sub> adsorption/desorption isotherm of (a) Ni<sub>2</sub>P/N,P-C; (b) N,P-C and the corresponding pore size distribution of (c) Ni<sub>2</sub>P/N,P-C; (d) N,P-C.



**Figure S10.** The well-resolved lattice fringe of Ni<sub>2</sub>P/N,P-C in Figure 2g were calculated based on Nano Measurer software analysis.

It can be seen from the above picture that the total length between the fifteen lattice stripes is 3.1 nm, so the distance between the two lattice stripes is 0.221 nm corresponding to the (111) crystal plane of Ni<sub>2</sub>P.



Figure S11. EDX spectrum of the as-fabricated Ni<sub>2</sub>P/N,P-C.

Figure S12. (a) XRD pattern of the residue of  $Ni_2P/N$ ,P-C after TGA measurement and (b) the corresponding TGA curve of  $Ni_2P/N$ ,P-C in air atmosphere.

To further figure out the mass loading of  $Ni_2P$  in the catalysts,  $Ni_2P/N$ ,P-C hybrids were tested by thermogravimetric analysis (TGA). The XRD spectra revealed that the corresponding residue is  $Ni_3(PO_4)_2$  originated from the oxidation of  $Ni_2P$ , which content can be determined as 34.23% (Supporting Information, Figure S12).



Figure S13. Raman spectra of Ni<sub>2</sub>P/N,P-C and N,P-C.



Figure S14. XPS spectra of C 1s for bulk Ni<sub>2</sub>P.

The Ni 2p for bulk Ni<sub>2</sub>P and Ni<sub>2</sub>P/N, P-C hybrid catalysts were put together and displayed in **Figure 2n**. Apparently, the Ni<sub>2</sub>P peaks in Ni<sub>2</sub>P/N, P-C hybrid show a positive shift of ~1.0 eV compared to Ni<sub>2</sub>P samples, indicating obviously charge transfer from Ni<sub>2</sub>P to the interface between Ni<sub>2</sub>P and N, P-C substrate, in consistence with the difference charge density result (Figure 1).



Figure S15. XPS spectra of C 1s for Ni<sub>2</sub>P/N,P-C.

The C 1s spectrum in **Figure S15** can be deconvoluted into four peaks of C-C (284.8 eV), C-N/C-P (285.9 eV), C-O (286.8 eV), C-C=O (287.8 eV) <sup>[4-6]</sup>.



**(b)** 



Figure S16. XPS spectra of (a) N 1s for Ni<sub>2</sub>P/N,P-C and (b) Ni 2p for Ni<sub>2</sub>P/N,P-C and Ni<sub>2</sub>P/N-C.

The N 1s region contains four peaks at the binding energy of 398.6 eV, 401.0 eV, 403.1 eV, 404.0 eV, corresponding to the pyridinic-N, pyrrolic-N, graphitic-N and oxidized-N<sup>[7,8]</sup>.

The Ni 2p XPS of Ni<sub>2</sub>P/N,P-C hybrid show a positive shift of ~1.0 eV compared to that of Ni<sub>2</sub>P/N-C samples (**Figure S16b**), indicating obviously charge transfer from Ni site in Ni<sub>2</sub>P/N,P-C to the interface between Ni<sub>2</sub>P and N,P-C substrate. In contrast, the interface charge aggregation in Ni<sub>2</sub>P/N-C sample originates from the P site and the N-C substrate rather than the Ni site.

Figure S17. Optical photograph of the three-electrode device for N<sub>2</sub>RR testing.

During electrocatalysis, N<sub>2</sub> was fed into the cathode cell at a specific flow, where protons and electrons transferred through 0.1 M HCl eletrolyte reacted with N<sub>2</sub> on the surface of catalyst to produce NH<sub>3</sub> (N<sub>2</sub> + 6H<sup>+</sup> + 6e<sup>-</sup>  $\rightarrow$  2NH<sub>3</sub>). As for N<sub>2</sub>RR in 0.1 M HCl, we list the reaction equation below:

Total: N<sub>2</sub> +  $3H_2O \rightarrow 2NH_3 + 3/2O_2$ 

Cathode:  $N_2 + 6H^+ + 6e^- \rightarrow 2NH_3$ 

Anode:  $3H_2O \rightarrow 3/2O_2 + 6H^+ + 6e^-$ 



Scheme S1. N<sub>2</sub>RR experimental procedures we utilized in this article.



**Figure S18.** Cyclic voltammetry (CV) curves of  $Ni_2P/N_P-C$  in both Ar-saturated (black line) and  $N_2$ -saturated (red line) 0.1 M HCl electrolyte at 50 mV s<sup>-1</sup>.

It can be clearly observed that the current density of  $Ni_2P/N$ ,P-C in  $N_2$ -saturated electrolyte were higher than that in Ar-saturated electrolyte at the same potential, indicating that  $Ni_2P/N$ ,P-C possess  $N_2RR$  catalytic activity.

In **Figure 3a**, as expected, when the applied potential is negative than -0.17 V, the current density of Ni<sub>2</sub>P in Ar saturated solution is much larger than that in N<sub>2</sub>, suggesting that Ni<sub>2</sub>P possess excellent HER performance while suppressing the occurrence of N<sub>2</sub>RR. In contrast, Ni<sub>2</sub>P/N,P-C and N,P-C are active for electrocatalytic reduction of  $N_2$  as they delivered the larger current density in  $N_2$  compared with that under Ar. Besides, the current density  $(j_{N2} - j_{Ar})$  of  $Ni_2P/N,P-C$  is larger than that of N,P-C at same potential. The above results indicate that  $Ni_2P/N,P-C$  is more active for the electrocatalytic reduction of  $N_2$  than  $Ni_2P$  and N,P-C, which verifies that the interaction between  $Ni_2P$  and N,P-C makes  $Ni_2P/N,P-C$  with the potential for  $N_2RR$ .



**Figure S19.** (a) UV-vis curves and (b) concentration-absorbance of  $NH_4Cl$  solution with a series of standard concentration (0-10 µg mL<sup>-1</sup>) in 0.1 M HCl. The absorbance at 655 nm was measured by UV-vis spectrophotometer. The standard curve showed good linear relation of absorbance with

NH<sub>4</sub>Cl concentration (y=0.1376x+0.0285, R<sup>2</sup>=0.9999); (c) UV-vis curves and (d) concentrationabsorbance of NH<sub>4</sub>Cl solution with a series of standard concentration (0-2  $\mu$ g mL<sup>-1</sup>) in 0.1 M HCl. The absorbance at 655 nm was measured by UV-vis spectrophotometer. The standard curve showed good linear relation of absorbance with NH<sub>4</sub>Cl concentration (y=0.1376x+0.0286, R<sup>2</sup>=0.9998); (e) UV-vis curves and (f) concentration-absorbance of NH<sub>4</sub>Cl solution with a series of standard concentration (0-2  $\mu$ g mL<sup>-1</sup>) in 0.2 M PBS. The absorbance at 655 nm was measured by UV-vis spectrophotometer. The standard curve showed good linear relation of absorbance with NH<sub>4</sub>Cl concentration (y=0.1356x+0.0486, R<sup>2</sup>=0.9987); (g) UV-vis curves and (h) concentrationabsorbance of NH<sub>4</sub>Cl solution with a series of standard concentration (0-2  $\mu$ g mL<sup>-1</sup>) in 0.1 M KOH. The absorbance at 655 nm was measured by UV-vis spectrophotometer. The standard curve showed good linear relation of absorbance with NH<sub>4</sub>Cl concentration (y=0.1035x+0.0395, R<sup>2</sup>=0.9981).



Figure S20. (a) UV-vis curves and (b) concentration-absorbance of  $N_2H_4$  solution with a series of standard concentration. The absorbance at 455 nm was measured by UV-vis spectrophotometer.

The standard curve showed good linear relation of absorbance with  $N_2H_4$  concentration (y=1.1158x+0.0252, R<sup>2</sup>=0.9999).



(d)



**Figure S21.** (a) UV-Vis spectra of electrolytes colored with indophenol indicator after 2h electrocatalytic reduction at different potentials; (b) Gas chromatography (GC) data of the amounts of  $H_2$  from the headspace of the cell for  $N_2RR$  on the  $Ni_2P/N,P-C$  catalyst in  $N_2$ -saturated 0.1 M HCl at various potentials; (c) The calculated FE of HER. According to the data obtained from the FE of  $N_2RR$ , the unaccounted value may be attributed to the capacitance of the carbon support; (d) NH<sub>3</sub> yield rate and Faradaic efficiency (blue line) of  $Ni_2P/N,P-C$  in different electrolyte at -0.2 V; (e) reaction kinetic studies of  $Ni_2P/N,P-C$ ,  $Ni_2P$  and N,P-C; (f-h) reaction kinetic studies of  $Ni_2P/N,P-C$  in different electrolyte.

The reaction kinetic were investigated by the formula:  $\ln(c_t/c_0)=kt+b$ , k represents the reaction rate constant (the slope of the curves represent k in this work).

**(b)** 

(c)

**Figure S22.** (a) UV-vis absorption spectra of the 0.1 M HCl electrolyte (after charging at different potentials for 2h) after incubated for 15 min at room temperature; nitrogen temperature-programmed desorption (N<sub>2</sub>-TPD) spectra of (b) Ni<sub>2</sub>P and (c) Ni<sub>2</sub>P/N,P-C.

As shown in **Figure S22b,c**, both Ni<sub>2</sub>P and Ni<sub>2</sub>P/N,P-C exhibited two peaks at 95 °C and 163 °C, which can be attributed to the physical adsorption of N<sub>2</sub>. The other desorption peak for Ni<sub>2</sub>P was located at 283 °C, which was assigned to the chemical adsorption of N<sub>2</sub>. By comparison, the peak for N<sub>2</sub> chemical adsorption was mainly located at 383 °C for Ni<sub>2</sub>P/N,P-C. As such, the binding strength of N<sub>2</sub> on Ni<sub>2</sub>P/N,P-C was stronger than that on Ni<sub>2</sub>P, indicating that the facilitated adsorption of N<sub>2</sub>, which result in high activity of Ni<sub>2</sub>P/N,P-C. Of note, compared to Ni<sub>2</sub>P, the total peak area of chemical desorption peak is much larger than that of physical adsorption for Ni<sub>2</sub>P/N,P-C, demonstrating that Ni<sub>2</sub>P/N,P-C is beneficial for the chemical adsorption of N<sub>2</sub>.





As expected, no N signal was detected in  $Ni_2P/P-C$  hybrids, indicating that  $Ni_2P/P-C$  was successfully synthesized.







**Figure S23.** (a) The FE and NH<sub>3</sub> yield rate of Ni<sub>2</sub>P/N,P-C; physically mixed Ni<sub>2</sub>P and N,P-C; (b) SEM images of Ni<sub>2</sub>P/P-C and the corresponding elemental mapping; (c) SEM images of Ni<sub>2</sub>P/N-C and the corresponding elemental mapping; (d) The FE of Ni<sub>2</sub>P/P-C and Ni<sub>2</sub>P/N-C; Difference charge densities of (e) Ni<sub>2</sub>P alloy supported on one-layer graphene with P-doped, where the isosurface value is set to be 0.003 e/Å<sup>3</sup> and the positive and negative charges are showed in yellow and cyan, respectively. Gray, green and pink balls represent the C, Ni and P atoms, respectively; (f) Planar-averaged electron density difference  $\Delta \rho(z)$  for (e) Ni<sub>2</sub>P alloy supported on one-layer graphene with P-doped. Inset is the 3D isosurface of the electron density difference, the gray areas represent Ni<sub>2</sub>P alloy of the electron density difference.

We also synthesized Ni<sub>2</sub>P/P-C and Ni<sub>2</sub>P/N-C as important control catalysts. It can be seen from **Figure S23b** that Ni<sub>2</sub>P with a diameter of about 700 nm is supported on the P-doped C substrate. Of note, no N element was observed, which can be attributed to the fact that we replaced melamine with carbon black during the preparation of Ni<sub>2</sub>P/P-C. In **Figure S23c**, N element is

uniformly dispersed on the carbon substrate and the diameter of the bulk Ni<sub>2</sub>P is larger than 5  $\mu$ m. When the applied potential is -0.2 V vs. RHE, the FE of Ni<sub>2</sub>P/N-C is 6.23%, which is superior than that of Ni<sub>2</sub>P/P-C (3.11%) (**Figure S23d**). In addition, we also calculated difference charge densities of Ni<sub>2</sub>P/P-C (**Figure S23e-f**). Compared to Ni<sub>2</sub>P/P-C, Ni<sub>2</sub>P/N-C transfers more electrons to the interface (more obvious electronic aggregation), making it rather more positively charged specie, which is consistent with the experimental results above. **Figure S24.** CV curves of (a) Ni<sub>2</sub>P/N,P-C; (b) Ni<sub>2</sub>P with different scan rates from 20 to 140 mV/s;  $\Delta J$  of catalysts plotted against scan rate at the potential of -0.1 V vs. RHE of (c) Ni<sub>2</sub>P/N,P-C and (d) Ni<sub>2</sub>P.

The electrochemical double-layer capacitance ( $C_{dl}$ ) was evaluated by CV curves in the non-Faradaic range of -0.2-0 V (vs. RHE) at the scan rate of 20, 40, 60, 80, 100, 120, 140 mV s<sup>-1</sup>, respectively. And the slope of corresponding plot of current density differences between the anodic and cathodic current density at -0.1 V vs. RHE versus the scan rate is twice of  $C_{dl}$ . And the electrochemical active surface areas (ECSA) was estimated based on the  $C_{dl}$  according to the following equation.

$$ECSA = \frac{Cdl}{0.040}$$

Where 0.040 represents the specific capacitance of a flat surface. Therefore, it can be inferred that the larger the slope of the line, the larger the ECSA of the catalyst.



Figure S25. Nyquist plots of electrochemical impedance spectra (EIS) of Ni<sub>2</sub>P/N,P-C and Ni<sub>2</sub>P.

As revealed by electrochemical impedance spectroscopy (EIS) measurements (Supporting Information, Figure S25), the Ni<sub>2</sub>P/N,P-C shows smaller semicircle and a higher slope, which demonstrate that the Ni<sub>2</sub>P/N,P-C has smaller electron transfer impedance and low ion diffusion/transfer resistance.



**Figure S26.** (a) UV-vis spectra of the electrolyte stained with indophenol indicator for the work electrode in  $N_2$ -saturated solution, without and after 2h electrolysis at the potential of -0.2 V in Arsaturated solution, without electrolysis in  $N_2$ -saturated solution; Example data sets were used to demonstrate calculation of Faradaic efficiency with and without background Ar measurements. (b) and (c) represent the NH<sub>3</sub> yield rate and FE of Ni<sub>2</sub>P/N,P-C tested in Ar-or N<sub>2</sub>-bubbled electrolyte (0.1 M HCl) with no electro-chemistry (represent by Ar and N<sub>2</sub>, respectively) and then Ar- or N<sub>2</sub>-bubbled electrolyte under applied potential (represent by Ar+Echem and N<sub>2</sub>+Echem, respectively).

The corresponding UV-Vis curve for pure carbon cloth in N<sub>2</sub>-saturated solution showed that no NH<sub>3</sub> was detected. We also performed electrolysis in Ar-saturated solution at -0.2 V vs. RHE and N<sub>2</sub>-saturated solution at open circuit potential (**Figure S26a**). Similarly, the corresponding UV-Vis absorption spectrum show a negligible signal indicating that no NH<sub>3</sub> is detected. All of these results demonstrate that detected NH<sub>3</sub> originated from the electrocatalytic N<sub>2</sub> reduction by Ni<sub>2</sub>P/N,P-C. In this part, we also started running Ar controls against N<sub>2</sub> tests to figure out the effect of ambient ammonia on the field of low-temperature electrocatalytic synthesis of ammonia. **Figure S26b** and **Figure S26c** prove that the presence of background NH<sub>3</sub>. And the calculated FE and yield rate of background NH<sub>3</sub> is 0.17% and 2.2  $\mu$ g h<sup>-1</sup> mg<sup>-1</sup><sub>Ni2P</sub>.





**Figure S27.** (a) <sup>1</sup>H NMR spectra (700 MHz) for <sup>15</sup>N<sub>2</sub>, N<sub>2</sub> and Ar were fed to the cell in the absence of polarization; (b) <sup>1</sup>H NMR spectra (700 MHz) for <sup>14</sup>NH<sub>4</sub><sup>+</sup> and <sup>15</sup>NH<sub>4</sub><sup>+</sup> produced from N<sub>2</sub> electrochemical reduction using N<sub>2</sub> and <sup>15</sup>N<sub>2</sub> as the feeding gas, respectively; (c) <sup>1</sup>H NMR spectra (700 MHz) of various <sup>15</sup>NH<sub>4</sub>Cl concentration; (d) Integral area (<sup>15</sup>NH<sub>4</sub><sup>+</sup> / C<sub>4</sub>H<sub>4</sub>O<sub>4</sub>) against various <sup>15</sup>NH<sub>4</sub>Cl concentration; (e) <sup>1</sup>H NMR spectra (700 MHz) of the electrolyte that reacted on Ni<sub>2</sub>P/N,P-C at -0.2 V for 2h under <sup>15</sup>N<sub>2</sub> conditions; (f) The <sup>15</sup>NH<sub>4</sub><sup>+</sup> concentration of the electrolyte that was quantitatively determined by <sup>1</sup>H NMR with external standards; (g) UV-vis curves and (h) concentration-absorbance of NH<sub>4</sub>Cl solution with a series of standard concentration (0-10  $\mu$ g mL<sup>-1</sup>) in 0.1 M HCl determined by Nessler's reagent method. The absorbance at 420 nm was measured by UV-vis spectrophotometer. The standard curve showed good linear relation of absorbance with NH<sub>4</sub>Cl concentration (y=0.0501x+0.0450, R<sup>2</sup>=0.9991).

Prior to use,  ${}^{15}N_2$ ,  $N_2$  and Ar were purified by passing through a an acid trap (0.05 M H<sub>2</sub>SO<sub>4</sub>). As shown in **Figure S27a**, when  ${}^{15}N_2$ ,  $N_2$  and Ar were fed to the cell in the absence of polarization, no  ${}^{15}NH_4^+$  peak and  ${}^{14}NH_4^+$  peak were observed, indicating that there is no NH<sub>3</sub> contamination and NOx in the feeding gases. Thus, we can eliminate other forms of nitrogen on experimental results. In order to quantify the ammonia produced more accurately, the analysis of <sup>15</sup>NH<sub>4</sub>Cl product was conducted by the <sup>1</sup> H nuclear magnetic resonance (<sup>1</sup> H NMR, Bruker, 700 MHz), a known quantity of maleic acid was added for quantitative analysis. And <sup>1</sup>H NMR spectra (700 MHz) of various <sup>15</sup>NH<sub>4</sub>Cl concentration were displayed in **Figure S27c**. As expected, integral area (<sup>15</sup>NH<sub>4</sub><sup>+</sup> / C<sub>4</sub>H<sub>4</sub>O<sub>4</sub>) against various <sup>15</sup>NH<sub>4</sub>Cl concentration show a good linear relationship (**Figure S27d**). In **Figure S27e**, the concentration of <sup>15</sup>NH<sub>4</sub>Cl lies between 0.1 µg mL<sup>-1</sup> and 0.2 µg mL<sup>-1</sup>. And we calculated the <sup>15</sup>NH<sub>3</sub> yield rate is 34.5 µg h<sup>-1</sup> mg<sup>-1</sup><sub>Ni2P</sub> in this work (**Figure S27f**). UV-Vis spectra of electrolytes colored with Nessler's reagent after 2h electrocatalytic reduction at -0.2V were displayed in **Figure S28a**. Similarly, the <sup>15</sup>NH<sub>4</sub>Cl concentration calculated based on Nessler's reagent method NH<sub>3</sub> yield rate is 34.4 µg h<sup>-1</sup> mg<sup>-1</sup><sub>Ni2P</sub> (**Figure S27g-h**). Since the concentrations of ammonia measured by <sup>1</sup> H NMR method and Nessler's reagent method are similar to the indophenol blue method, the above comparative experiments all strongly prove that our Ni<sub>2</sub>P/N,P-C can achieve high FE and ammonia yields.



**Figure S28.** (a) UV-Vis spectra of electrolytes colored with Nessler's reagent after 2h electrocatalytic reduction at -0.2V; (b) The chronoamperometric curves of  $Ni_2P/N_3P-C$  in  $N_2$ -saturated 0.1 M HCl electrolyte at various potentials for 24h.

**Figure S29.** FESEM images of Ni<sub>2</sub>P/N,P-C in low (a) and high (b) resolution after electrolysis for 2h at -0.2 V vs. RHE.

**Figure S30.** XPS spectra of (a) Ni 2p and (b) P 2p for Ni<sub>2</sub>P/N,P-C after electrolysis for 2h at -0.2 V vs. RHE.


Figure S31. XRD patterns of Ni<sub>2</sub>P/N,P-C after electrolysis for 2h at -0.2 V vs. RHE.



Figure S32. The fully optimized structure of (a)  $Ni_2P(111) / N,P-C$  and (b)  $Ni_2P(111)$ .

We considered a Ni<sub>2</sub>P (111) surface on a N,P co-doped graphene (N,P-C) monolayer to simulate the Ni<sub>2</sub>P nanoparticles supported by the carbon substrate. **Figure S32a** presents the fully optimized structure of Ni<sub>2</sub>P (111) / N,P-C. Of note, we chose pyridinic N and pyrrolic N doping into carbon substrate in this work for two reasons: first, based on the XPS analysis (**Supporting Information, Figure S16**), the contents of pyridinic N and pyrrolic N account for more than 80% of the total nitrogen content. Selective incorporation of pyridinic N and pyrrolic N into the carbon substrate can reduce the difficulty of theoretical calculations; More importantly, it has been reported that pyridinic N and pyrrolic N are the catalytic active sites in N-doped carbon for N<sub>2</sub>RR<sup>[9]</sup>. For comparison, we also construct the Ni<sub>2</sub>P (111) structure without the graphene monolayer (**Supporting Information, Figure S32b**).



**(b)** 

(c)

**(a)** 

(d)



Figure S33. (a) The front view and (b) side view of optimized structure of  $N_2$  adsorption on the  $Ni_2P$  (111) / N,P-C surface for the end-on and (c) the front view and (d) side view for side-on

configurations. Gray, blue, green and pink balls represent the C, N, Ni and P atoms, respectively.

As depicted in **Figure S33**, end-on and side-on configurations are energetically favorable for the chemisorption of N<sub>2</sub> molecule on Ni<sub>2</sub>P (111) / N,P-C surface. As expected, the binding strength between N<sub>2</sub> and Ni<sub>2</sub>P are about -0.58 eV for the end-on configuration and -0.13 eV for the side-on configuration, respectively. When taking account of  $\Delta E_{ZPE}$  and entropy, the  $\Delta G$  values for the N<sub>2</sub> adsorption on the Ni<sub>2</sub>P (111) / N,P-C surface are -0.50 eV (end-on configuration) and -0.05 eV (side-on configuration), respectively.

**(a)** 

**(b)** 



**Figure S34.** (a) The front view and (b) side view of optimized structure of  $N_2$  adsorption on the P site of  $Ni_2P$  (111) / N,P-C surface via the end-on configurations. Gray, blue, green and pink balls represent the C, N, Ni and P atoms, respectively.



(c)

(d)





(f)





(h)



(i)





(j)



**Figure S35.** (a) The front view and (b) side view of optimized structure of  $N_2$  adsorption on Ni<sub>2</sub>P (111) / N,P-C surface via the end-on configurations and the corresponding difference charge density from (c) the front view and (d) side view. The isosurface value is set to be 0.001 e/Å<sup>3</sup> and the positive and negative charges are showed in yellow and cyan, respectively. Gray, blue, green and pink balls represent the C, N, Ni and P atoms, respectively; (e-k) The models of different intermediates adsorbed on the Ni<sub>2</sub>P/N,P-C based on alternating mechanisms and the corresponding charge distribution based on Difference charge density analysis.

In order to more clearly illustrate that N,P-C substrate regulates the electronic distribution of the catalyst when  $N_2$  is chemically adsorbed at the Ni site, we labeled the charge for each atom in Figure 5c. It can be clearly seen from **Figure S35e-k** that the each atom of the  $N_xH_y$  and  $Ni_2P$  units undergo significant charge changes while N,P-C substrate is always a negatively charged substance. Electronic storage i.e. negatively charged N,P-C substrate also exhibits excellent

regulation ability to regulate electronic redistribution of Ni<sub>2</sub>P/N,P-C when N<sub>2</sub> is chemically adsorbed at the Ni site. Evidently, without N,P-C substrate, pure Ni<sub>2</sub>P can not chemisorb N<sub>2</sub>, let alone achieve N<sub>2</sub> activation. In contrast, the N,P-C substrate in Ni<sub>2</sub>P/N,P-C hybrids not only accelerates the adsorption of N<sub>2</sub> on the positively charged Ni sites, but also guarantees the generate of activated N<sub>x</sub>H<sub>y</sub> intermediates. In other words, the total charge of N<sub>x</sub>H<sub>y</sub> intermediates adsorbed Ni<sub>2</sub>P/N, P-C does not change. Considering Ni<sub>2</sub>P serves as transmitter to transfer charge between N<sub>x</sub>H<sub>y</sub> species and N, P-C sheets and N, P-C species are always negatively charged species, the electrons injection and output of N<sub>x</sub>H<sub>y</sub> intermediates benefit from the presence of N,P-C substrate to regulate electronic redistribution of Ni<sub>2</sub>P/N,P-C when N<sub>2</sub> is chemically adsorbed at the Ni site. (d)

**(e)** 

**(f)** 

**Figure S36.** Optimized structure of (a) H adsorption and (b)  $N_2$  adsorption on the Ni<sub>2</sub>P (111) surface, and the corresponding (c) Free energy diagrams for H and  $N_2$  adsorption; Optimized structure of (d) H adsorption and (e)  $N_2$  adsorption on the Ni<sub>2</sub>P (111) / N,P-C surface, and the corresponding (f) Free energy diagrams for H and  $N_2$  adsorption. Gray, blue, green, white and pink balls represent the C, N, Ni, H and P atoms, respectively.

Compared to free energy for \*H formation on Ni<sub>2</sub>P (111) (-0.44 eV), Ni<sub>2</sub>P (111) model is much less favorable (0.14 eV) for \*N<sub>2</sub> formation, indicating that Ni<sub>2</sub>P (111) will be less covered by \*N<sub>2</sub> on the active sites (**Supporting Information, Figure S36a-c**). As excepted, the Ni<sub>2</sub>P (111) / N,P-C system will perform a rather energetically favorable for \*N<sub>2</sub> formation (-0.50 eV), which is lower than that of \*H formation (0.05 eV) (**Supporting Information, Figure S36d-f**).



Figure S37. Free energy diagrams for N<sub>2</sub> and N<sub>2</sub>H adsorbed on Ni<sub>2</sub>P and Ni<sub>2</sub>P/N,P-C.

As reported by Guo *et al* and Yu *et al*, the key design strategy for a potential N<sub>2</sub>RR electrocatalyst should enable a good density of active catalytic sites, which can facilitate the adsorption and activation of N<sub>2</sub> molecules<sup>[11-13]</sup>. Thus, we not only considered the adsorption ability of Ni<sub>2</sub>P and Ni<sub>2</sub>P/N,P-C for \*N<sub>2</sub>, but also calculated the driving force of different catalysts for \*N<sub>2</sub>H formation. As shown in **Figure S37**, the Gibbs free energy uphill for the production of \*N<sub>2</sub>H species is 0.17 eV and 0.35 eV for Ni<sub>2</sub>P/N,P-C and Ni<sub>2</sub>P, respectively, in this work. Both **Figure S36** and **Figure S37** indicate that Ni<sub>2</sub>P/N,P-C is not only more favorable for selective adsorption of N<sub>2</sub> but also requires less driving force to form N<sub>2</sub>H compared to that of Ni<sub>2</sub>P. These results prove that Ni<sub>2</sub>P/N,P-C can effectively facilitate the adsorption and activation of N<sub>2</sub> molecules. Additionally, although the driving force to form H<sub>2</sub> (0.05 eV) is smaller than form \*N<sub>2</sub>H (0.17 eV), it is different to form \*H in the first step than to form \*N<sub>2</sub>H (**Figure S36f**). This ensures the subsequent reaction of N<sub>2</sub>RR while suppresses HER on Ni<sub>2</sub>P/N,P-C. **Table S2.** Comparison of the electrocatalytic activity of  $Ni_2P/N$ , P-C to produce  $NH_3$  through  $N_2RR$  with previously reported  $N_2RR$  electrocatalysts.

Catalysts	Electro lyte	Potent ial (V vs. RHE)	Faradaic efficienc y (%)	NH <sub>3</sub> yield rate	Reference
Ni <sub>2</sub> P/N,P- C	0.1 M HCl	-0.2	17.21	34.4 μg h <sup>-1</sup> mg <sup>-1</sup> <sub>Ni2P</sub> 11.8 μg h <sup>-1</sup> mg <sup>-1</sup> <sub>cat</sub>	This work
NiCo@Ni CoO 2 Core@She ll Nanoparti cles NiCo@Ni CoO 2 Core@She ll Nanoparti cles SA- Mo/NPC	0.1 M HCl	-0.25	6.8±0.3	31.5±1.2 μg h <sup>-1</sup> mg <sup>-</sup> <sup>1</sup> cat	Angew Chem. Int Ed., 2019, 58, 2321-2325
B <sub>4</sub> C	0.1 M HCl	-0.75	15.95	26.57 μg h <sup>-1</sup> mg <sup>-1</sup> cat	Nat. Commun., 2018, 9, 3485
Bi <sub>4</sub> V <sub>2</sub> O <sub>11</sub> / CeO <sub>2</sub>	0.1 M HCl	-0.2	10.16	23.21 μg h <sup>-1</sup> mg <sup>-1</sup> cat	Angew Chem. Int. Ed. 2018, 57, 6073

Boron- doped graphene	0.05 M H <sub>2</sub> SO <sub>4</sub>	-0.5	10.8	9.8 μg h <sup>-1</sup> cm <sup>-2</sup>	Joule 10.1016/j.joule.2 018.06.007
PCN	0.1 M HCl	-0.2	11.59	8.09 μg h <sup>-1</sup> mg <sup>-1</sup>	Angew Chem. Int. Ed. 2018, 57, 10246
MoS <sub>2</sub>	0.1 M HCl	-0.5	0.096	8.48×10 <sup>-11</sup> mol s <sup>-1</sup> cm <sup>-2</sup>	Adv. Mater., 2018, 30, 1800191
NPC	0.05 M H <sub>2</sub> SO <sub>4</sub>	-0.9	1.42	27.2 μg h <sup>-1</sup> mg <sup>-1</sup>	ACS Catal., 2018, 8, 1186
Nb2O5 nanofiber	0.1 M HCl	-0.55	9.26	43.6 μg h <sup>-1</sup> mg <sup>-1</sup>	Nano Energy., 2018, 52, 264
ZIF- derived carbon	0.05 M H <sub>2</sub> SO <sub>4</sub>	-0.3	10.20	23.8 μg h <sup>-1</sup> mg <sup>-1</sup>	Nano Energy., 2018, 48, 217
a- Au/CeO <sub>x</sub> - RGO	0.1 M HCl	-0.2	10.1	8.3 μg h <sup>-1</sup> mg <sup>-1</sup>	Adv. Mater., 2017, 29, 1700001

Au cluster/Ti O <sub>2</sub>	0.1 M HCl	-0.2	8.11	21.4 μg h <sup>-1</sup> mg <sup>-1</sup>	Adv. Mater., 2017, 29, 1606550
MoO <sub>3</sub>	0.1 M HCl	-0.3	1.9	29.43 μg h <sup>-1</sup> mg <sup>-1</sup>	J. Mater. Chem. A., 2018, 6, 12974
Mo <sub>2</sub> N	0.1 M HCl	-0.3	1.15	3.01×10 <sup>-10</sup> mol s <sup>-1</sup> cm <sup>-2</sup>	Chem. Commun., 2018, 54, 8474-8477
Pd/C	0.1 M PBS	0.1	8.2	4.5 μg h <sup>-1</sup> mg <sup>-1</sup> cat	Nat. Commun., 2018, 9, 1795
Fe <sub>2</sub> O <sub>3</sub> - CNT	0.1 M KHC O3	-2 V vs. Ag/A gCl	4.9	2.2×10 <sup>-3</sup> g h <sup>-1</sup> cm <sup>-2</sup>	Angew Chem. Int. Ed. 2017, 56, 2699
Pd <sub>0.2</sub> Cu <sub>0.8</sub> /rGO	0.1 М КОН	-0.2	4.5	2.8 μg h <sup>-1</sup> mg <sup>-1</sup>	Adv. Energy Mater. 2018, 8, 1800124
Au film	0.1 M KOH	-0.5	<1	$\begin{array}{c} \textbf{3.84}\times \textbf{10}^{-12} \text{ mol} \\ \textbf{cm}^{-2} \text{ s}^{-1} \end{array}$	J. Am. Chem. Soc. 2018, 140, 1496
Au nanorods	0.1 M KOH	-0.2	4.02	1.648 µg h <sup>-1</sup> cm <sup>-2</sup>	Adv. Mater. 2017, 29,

Experime Locati nts on		Durness of the tests or controls	NH <sub>3</sub> yield rate
		Purpose of the tests of controls	$(\mu g h^{-1} m g^{-1}_{Ni2P})$
Sample-Ar- echem	Figure S 26	Check the contaminants from potential-dependent leaching/decomposition of the catalysts, impurities (such as NO <sub>3</sub> <sup>-</sup> ) in the electrolyte chemicals, etc.	2.2
Sample-Ar- ambient	Figure S 26	Check the ammonia contaminants from the inlet N <sub>2</sub> /Ar gas, leakage from the atmosphere, ammonia adsorbed on electrodes or reactors, impurities (such as	negligible
Sample-N <sub>2</sub> - ambient	Figure S 26	$\rm NH_4^+$ ) in the electrolyte chemicals, etc.	negligible
Bare WE- N <sub>2</sub> -echem	Figure S 26a	Check the contribution from the working electrode substrate (activity or contaminants), the contaminants from the inlet $N_2$ gas (such as NOx), impurities (such as NO <sub>3</sub> <sup>-</sup> ) in the electrolyte chemicals, etc.	negligible
Sample-N <sub>2</sub> - echem	Figure S 26	Study the N <sub>2</sub> RR activity of electrocatalysts	34.4
Sample- <sup>15</sup> N <sub>2</sub> - ambient	Figure S 27	Check the contaminants from the inlet ${}^{15}N_2/N_2$ gas (such as ${}^{15}NH_3$ ), etc.	negligible
Sample- <sup>14</sup> N <sub>2</sub> - ambient	Figure S 27		negligible
Sample- <sup>15</sup> N <sub>2</sub> -echem	Figure S 27	Confirm the N <sub>2</sub> RR activity of electrocatalysts, and check the potential-dependent leaching /decomposition of the catalysts, etc.	34.5

## Table S3. Electrochemical tests and controls to rigorously evaluate the $N_2RR$ activity<sup>[14]</sup>

In order to eliminate any ammonia and other contaminants, all components of the electrochemical

cell were firstly soaked in 0.05 M H<sub>2</sub>SO<sub>4</sub> solution for 24 h and then washed copiously with fresh ultrapure water before N<sub>2</sub>RR tests. Besides, all labware (needles, vials, pipet tips, containers, etc.) utilized in this work were also treated by 0.1 M H<sub>2</sub>SO<sub>4</sub> solution and water. Electrodes were used either immediately after preparation or kept in vacuum before being used in electrochemical experiments to avoid excessive oxidation by air oxygen and contamination with ambient ammonia or other nitrogen-containing species. To remove the impurities in the inlet gas, such as NH<sub>3</sub> and NO<sub>X</sub>, the prepurification of high-purity N<sub>2</sub> and Ar by passing through a saturator filled with 0.05 M H<sub>2</sub>SO<sub>4</sub> solution to remove any possible contaminants<sup>[15,16]</sup>. Due to ubiquitous contaminants, a set of control experiments have been strongly recommended by several groups,<sup>[17-19]</sup> typically including non-electrochemical and electrochemical experiments in both  $N_{2} \mbox{ and } Ar. \mbox{ As shown in }$ Table S3, electrochemical experiments in Ar (sample-Ar-echem) investigate the contaminants from leaching/decomposition of the catalysts or impurities (such as NO<sub>3</sub><sup>-</sup> in the electrolyte chemicals), while the non-electrochemical experiments conducted by direct bubbling (sample-Arambient, sample-N2-ambient) evaluate the contaminants from the inlet gas, leakage from the atmosphere, or ammonia adsorbed on electrodes/reactors. The NH<sub>3</sub> yield rate of sample-Ar-echem is 2.2 µg h<sup>-1</sup> mg<sup>-1</sup><sub>Ni2P</sub>, while the value for sample-Ar-ambient and sample-N<sub>2</sub>-ambient is negligible. These results demonstrate that pretreatment of electrochemical devices and pre-purification of gases play an important role in reducing the interference of environmental factors on the experiment. The contribution from the working electrode substrate should also be electrochemically studied in  $N_2$  (bare WE- $N_2$ -echem). The negligible  $NH_3$  yield rate exclude the contribution of working electrode substrate to N<sub>2</sub>RR. Besides, isotopic labelling experiments ( $^{15}N_2$ ) are mandatory for the verification of ammonia produced by N<sub>2</sub>RR, especially for nitrogencontaining catalysts. Similar to other comparison experiments, the prepurification of high-purity  $^{15}N_2$  by passing through a saturator filled with 0.05 M H<sub>2</sub>SO<sub>4</sub> solution to remove any possible contaminants (such as <sup>15</sup>NH<sub>3</sub> and NO<sub>X</sub> in <sup>15</sup>N<sub>2</sub> gas). The negligible NH<sub>3</sub> yield rate for sample-<sup>15</sup>N<sub>2</sub>ambient and sample-15N2-ambient proven that the impurities in the gas have been successfully removed. Moreover, the total NH<sub>3</sub> yield rate for <sup>15</sup>N<sub>2</sub> tests is quantitatively consistent with the corresponding N<sub>2</sub> tests under the same condition. The results in this work were supported by indophenol blue method, Nessler's reagent method and <sup>1</sup>H nuclear magnetic resonance method, which were expected to be more convincing and reliable<sup>[20-22]</sup>.

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