Supporting Information(SI):

# Co, N-codoped porous vanadium nitride nanoplates as superior bifunctional electrocatalysts for hydrogen evolution and oxygen reduction reactions

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**Electrochemically Active Surface Area.**

In order to estimate the effective surface area of the electrodes, cyclic voltammograms of catalysts in 1 M KOH was first obtained when there is no Faraday current. The scan speed was set as 10, 20, 40, 60, 80, 100 and 120 mV/s, respectively. When the difference in current density (*J*) between the anodic and cathodic sweeps ($J_{anodic}$ - $J_{cathodic}$) at 0.95 V against the scan rate was plotted, a linear relationship between the two was obtained (Fig. 6D). ECSA can be estimated according to the two following formulas [S1]:

$$C_{dl} = i_c/v \quad (1)$$

Where $i_c$ represents the charging current, v represents the scan rate.

$$ECSA = C_{dl}/C_s \quad (2)$$

A $C_s$ value of 0.040 $mFcm^{-2}$ was thus adopted according to previous reports [S2].

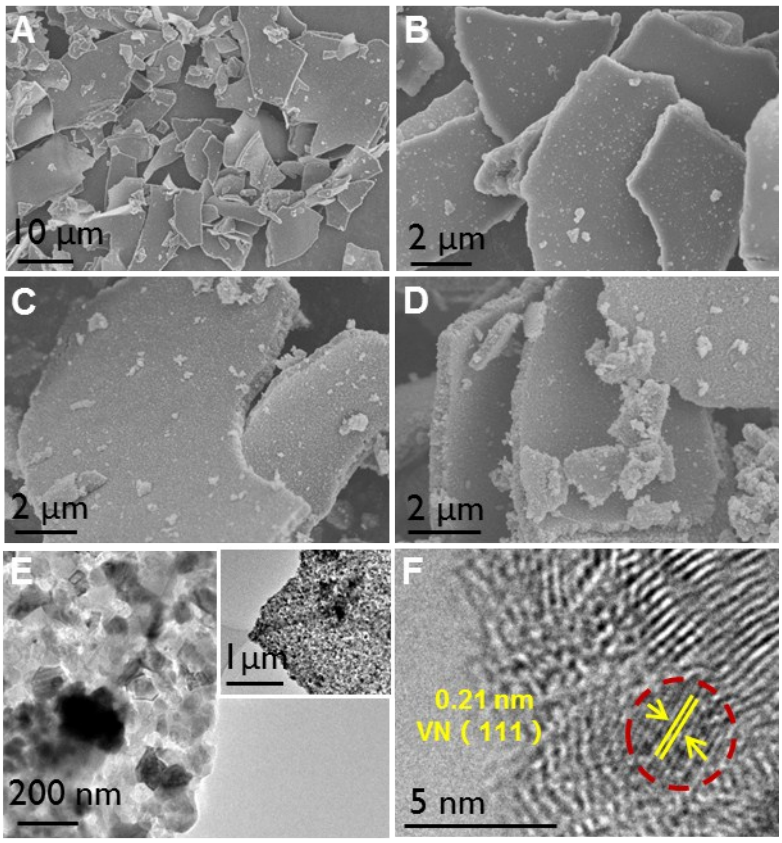



**Fig. S1** (A-D) SEM, (E) TEM and (F) HRTEM images of VCoN.

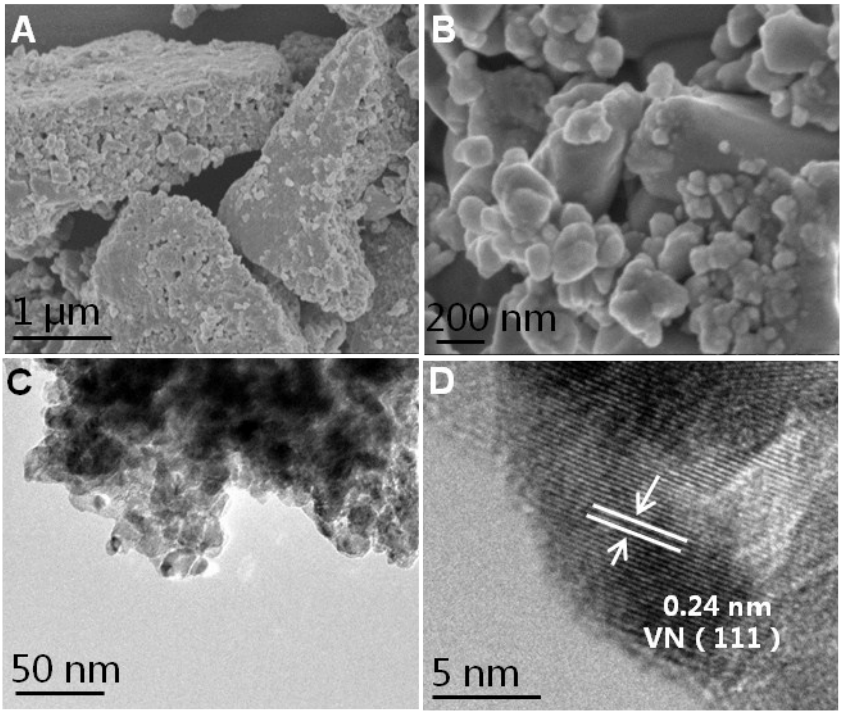
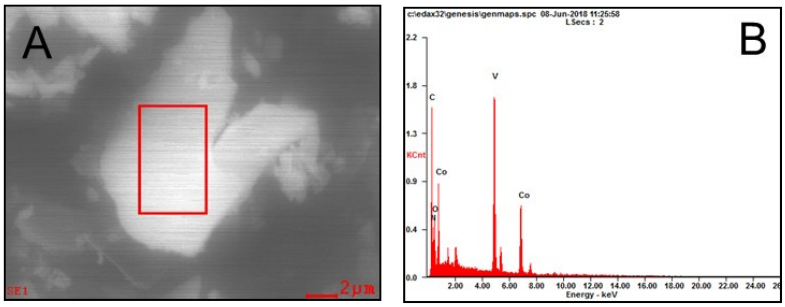



**Fig. S2** (A-B) SEM images, (C-D) TEM and HRTEM images of pure VN.




C

| *Element* | *Wt%* | *At%* |
|---|---|---|
| ***CK*** | 25.52 | 43.25 |
| ***NK*** | 14.74 | 21.42 |
| ***OK*** | 14.37 | 18.29 |
| ***VK*** | 25.13 | 10.04 |
| ***CoK*** | 20.24 | 06.99 |
| ***Matrix*** | Correction | ZAF |

**Fig. S3** EDX results of VCoN (obtained by SEM).

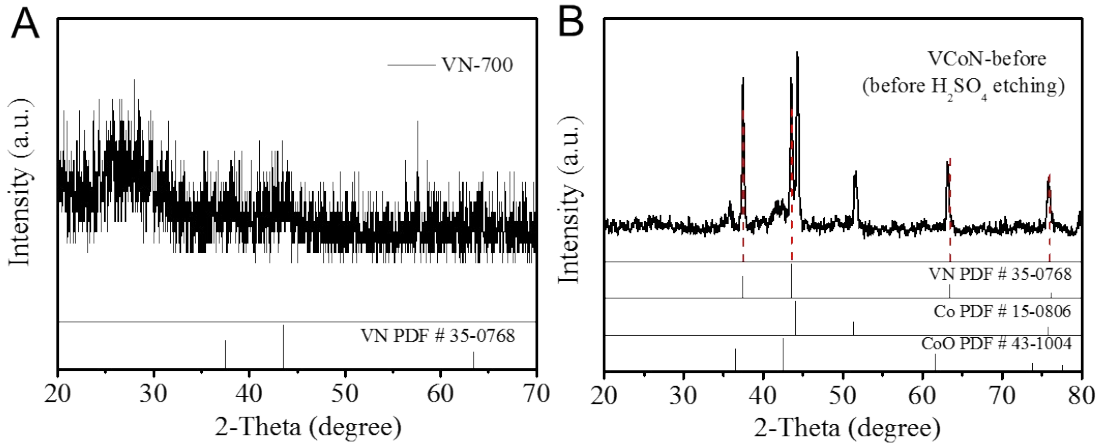



**Fig. S4** XRD patterns of (A) VN-700 and (B) VCoN-before.

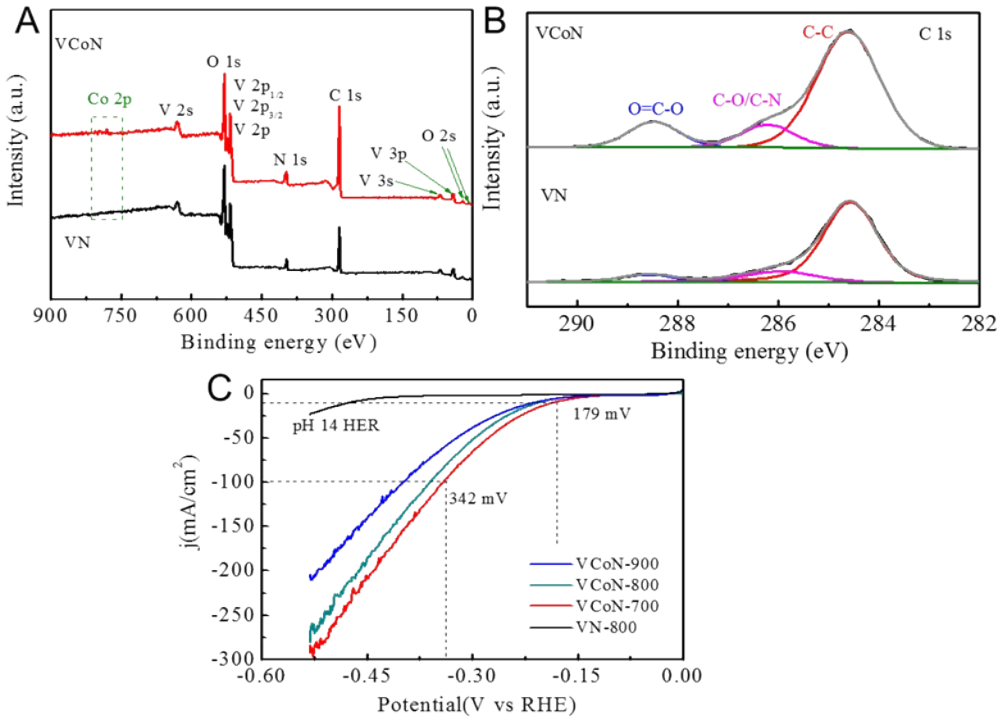



**Fig. S5** (A) Survey, (B) C 1s XPS spectra of VN and VCoN, (C) Polarization curves of samples for HER.

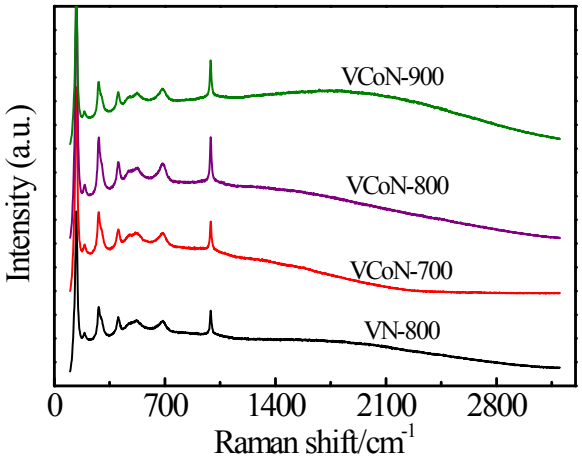



**Fig. S6** Raman spectra of samples.

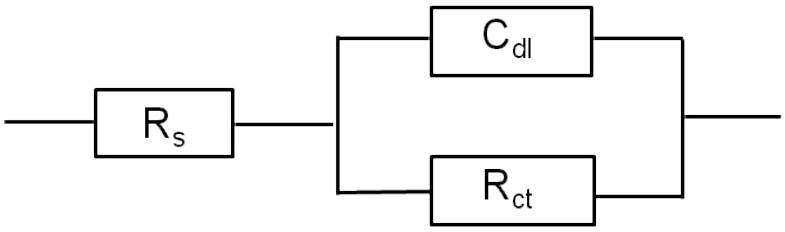



**Fig. S7** Electrical equivalent circuit used to simulate the Nyquist plots in Fig. 6C, where $R_s$ is the electrolyte resistance, $R_{ct}$ is the charge-transfer resistance, and $C_{dl}$ represents the double-layer capacitance.

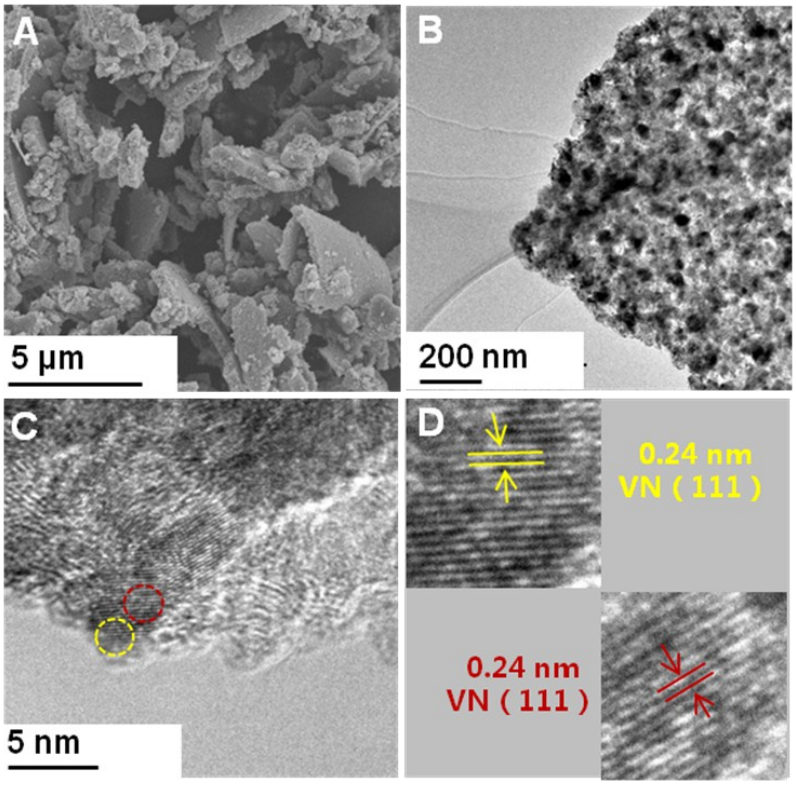



**Fig. S8** (A): SEM, (B-C) TEM and (D): HRTEM images of VCoN-700 after the HER stability test of i-t curve for 100 h at pH 14.

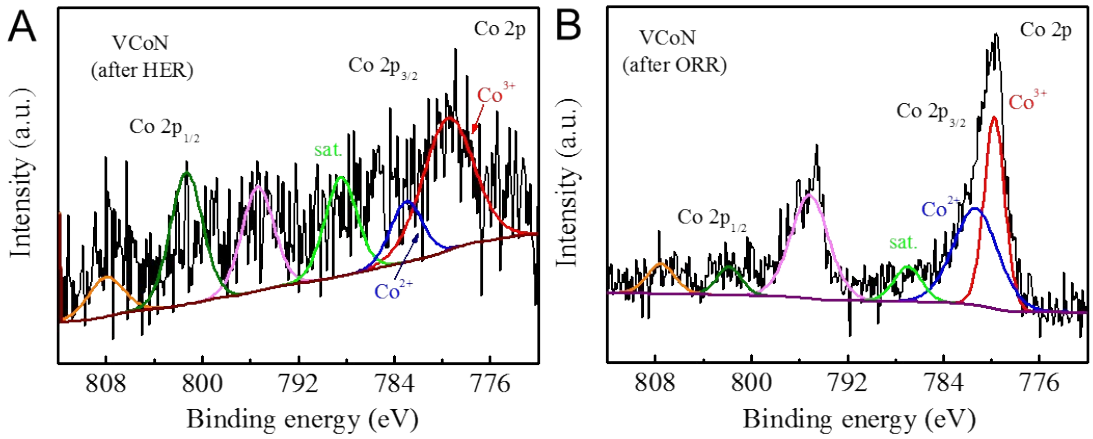



**Fig. S9** Co 2p high-revolution XPS spectra of VCoN after (A) HER and (B) ORR stability test.

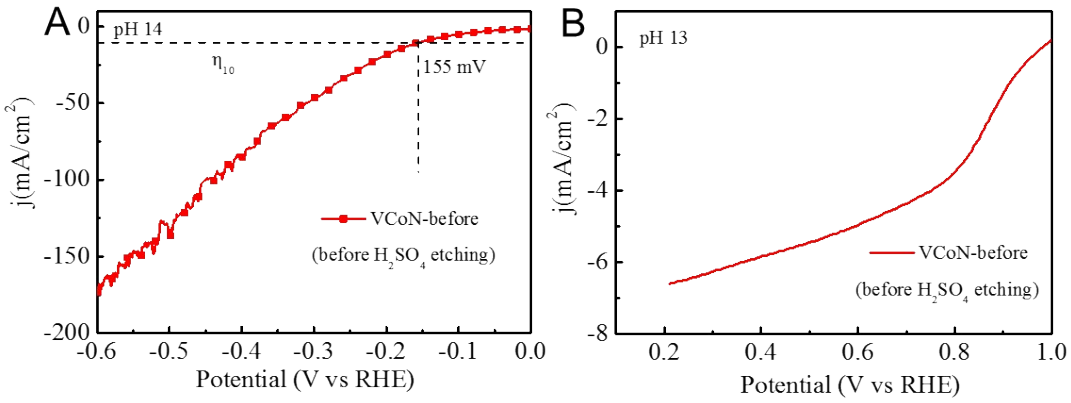



**Fig. S10** (A) Polarization curve for HER, (B) LSV curve at a sweep rate of 5 mV $s^{-1}$ and a rotation speed of 1600 rpm for ORR of VCoN-before.

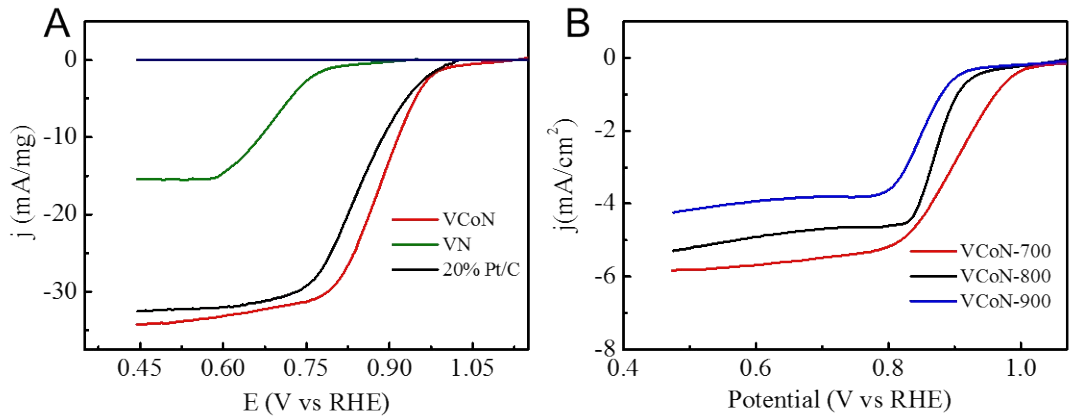



**Fig. S11** (A) RRDE curves of VCoN, 20% Pt/C and VN, (B) LSV curves of VCoN samples obtained at different synthesis temperatures at a sweep rate of 5 mV $s^{-1}$ and a rotation speed of 1600 rpm for ORR.

**Table S1** Comparisons of VN-based electrocatalysts for ORR, as well as bifunctional electrocatalysts for both HER and ORR.

| Catalyst | Overpotential (mV, at 10 mA $cm^{-2}$) | Stability test (HER) | Potential (V, at half peak) | Stability test (ORR) | Reference |
|---|---|---|---|---|---|
| **VCoN** | **179** | **100 h** | **0.91** | **2000 cycles** | **This work** |
| **20% Pt/C** | **43** | **-** | **0.87** | **2000 cycles** | |
| **$V_{0.95}Co_{0.05}N$ MFs** | - | - | 0.8 | 25000 s | *Appl. Mater. Interfaces.* 2018, **10**, 11604-11612 |
| **NGT-$Co_{35}V_{65}$-45-900** | - | - | 0.81 | 10000 cycles | *Nanoscale.* 2018, **10**, 4311-4319 |
| **$Mo_2C$@NC nanomesh** | 36 | 16 h | 0.872 | 10 h | *Adv. Funct. Mater.* 2018, **18**, 1705967 |
| **$Mo_2C$/NPC NFs** | 134 | 10 h | 0.77 | 10 h | *Carbon.* 2017, **114**, 628-634 |
| **Co, N-CT** | 106 | 20 h | 0.85 | 20 h | *J. Mater. Chem. A*. 2018, **35**, 17067-17074 |
| **Fe-CACNF** | 350 | ~13 h | 0.83 | ~30 h | *J. Mater. Chem. A*. 2017, **5**, 7507-7515 |
| **A-PBCCF-H** | 225 | 12 h | 0.76 | 12 h | *Nano Energy*. 2017, **32**, 247-254 |
| **BCN** | 216 | 8 h | 0.82 | ~8 h | *J. Mater. Chem. A*.2016, **42**, 16469-16475 |

**References**

[S1] CCL. McCrory, S. Jung, Peters Jonas C. and Jaramillo Thomas F., *J. Am. Chem. Soc,*. 2013, **135**, 16977.

[S2] Y. Zhang, Q. Shao, Y. C. Pi, J. Guo, X. Q. Huang, *Small,* 2017, **13**, 1700355.