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Porous Single-Crystalline Vanadium Nitride Octahedron with Unique Electrocatalytic Performance

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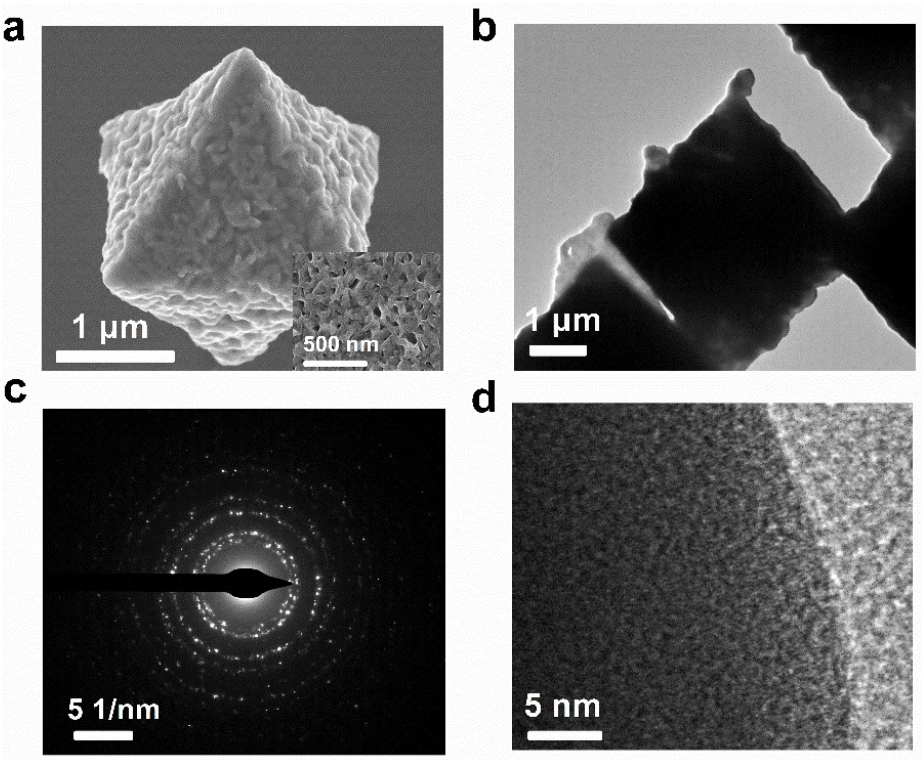


Figure S1. (a) SEM image; (b) TEM image; (c) SAED pattern and (d) Cs-corrected HRTEM image of PPC-VN.

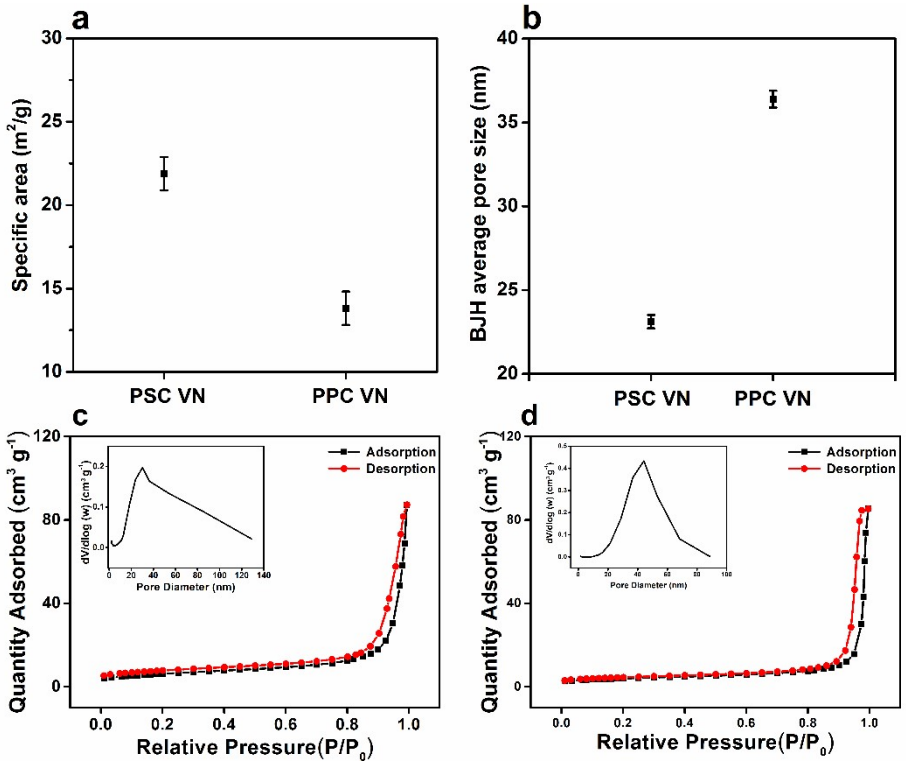
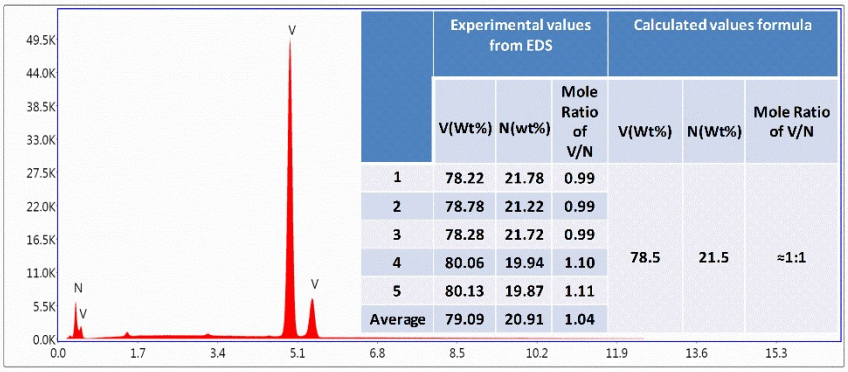


Figure S2. (a, b) The surface specific area and BJH average pore size of PSC-VN and PPC-VN. N_2 adsorption-desorption isotherms and (inset) the corresponding pore diameter distribution of porous single crystal micron particles, (c) PSC-VN (d) PPC-VN.



	Experimental values from EDS			Calculated values formula		
	V(Wt%)	N(wt%)	Mole Ratio of V/N	V(Wt%)	N(Wt%)	Mole Ratio of V/N
1	78.22	21.78	0.99	78.5	21.5	≈1:1
2	78.78	21.22	0.99			
3	78.28	21.72	0.99			
4	80.06	19.94	1.10			
5	80.13	19.87	1.11			
Average	79.09	20.91	1.04			

Figure S3. The element analysis of PSC-VN. No oxygen residual is observed from EDS elemental analysis. The mole ratio between V and N is approximately at 1.

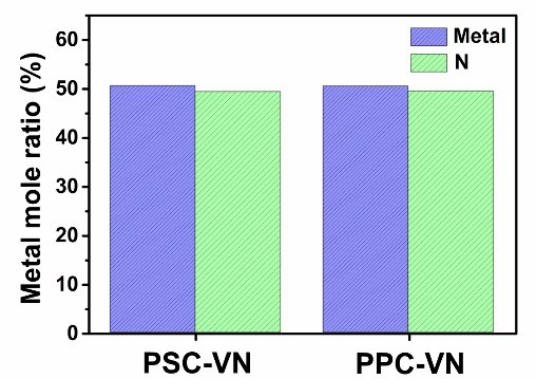


Figure S4. ICP and CA results. Mole ratio between metal and nitrogen in PSC-VN and PPC-VN.

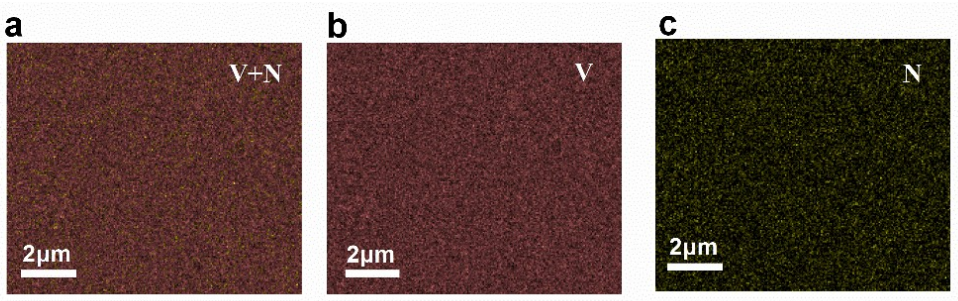


Figure S5. EDS mapping images of VN.

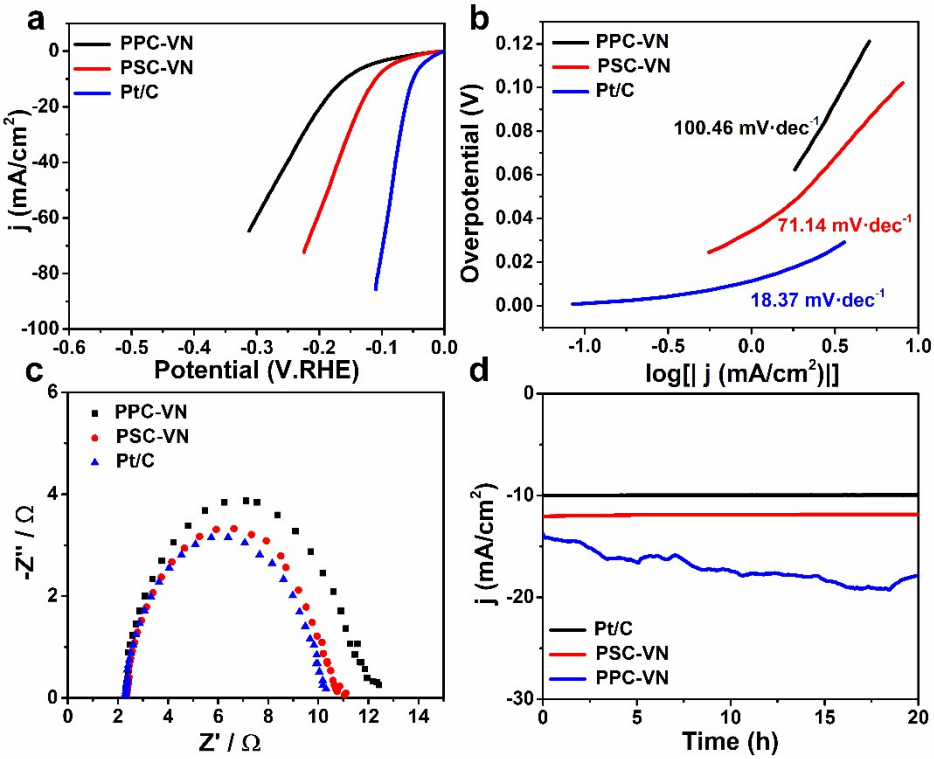


Figure S6. Pt/C (20 wt%), PSC-VN and PPC-VN catalysts toward HER. (a) LSV curves in 0.5 mol·L^{-1} H_2SO_4 solution with a scan rate of 10 mV/s; (b) Tafel plots and (**c**) the EIS Nyquist plots; (d) Long-standing tolerance test of the Pt/C (20%) at -0.05 V $_{VS.}$RHE, PSC-VN at -0.1 V $_{VS.}$ RHE and PPC-VN catalysts at -0.2 V $_{VS.}$ RHE for 20 h in 0.5 mol·L^{-1} H_2SO_4 solustion.

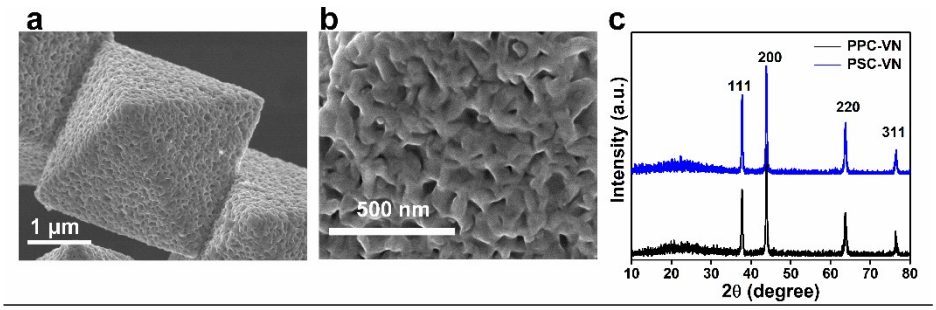


Figure S7. Crystal structure after stability test. (a, b) SEM image of the catalyst after the stability test; (c) The XRD of the catalysts after the stability test.

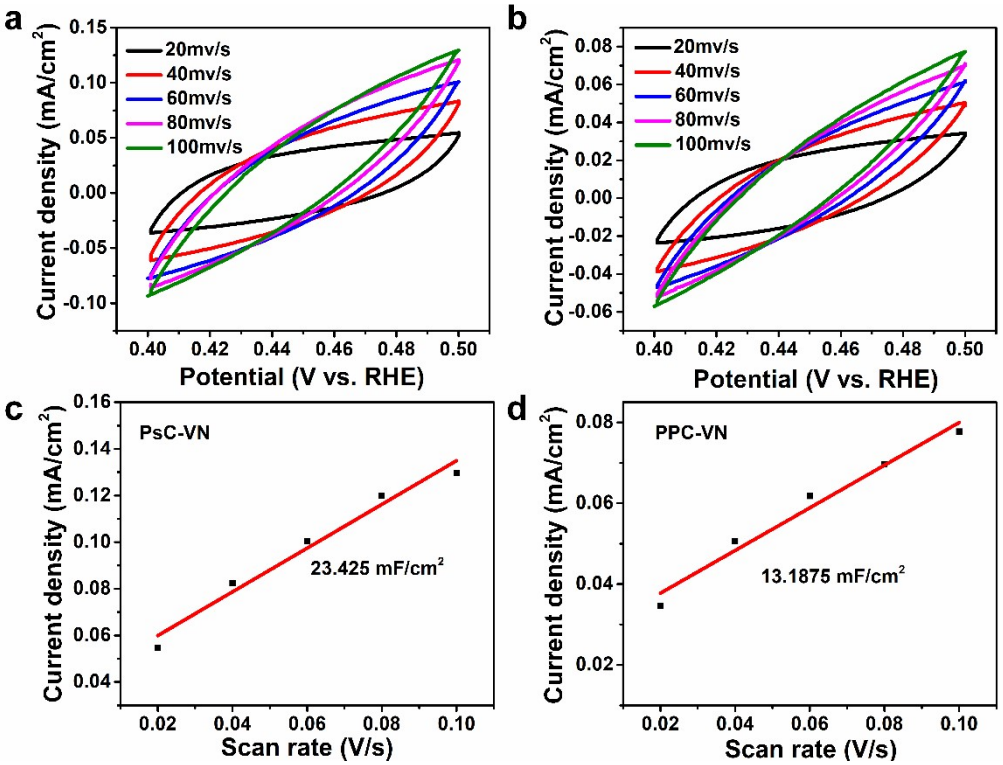


Figure S8. CVs of (a) PSC-VN and (b) PPC-VN octahedron catalysts at 20-100 mV/s in 1.0 mol·L^{-1} KOH solution; (c-d) Plots providing the C_{dl} value of PSC-VN and PPC-VN catalysts, respectively.

Table S1. The summary of the performance of difference catalysts for HER

Catalyst	η(mV)at j=10mA·cm^{-2}	Tafel slope (mV·dec^{-1})	Electrolyte	References
VN PSC	74.67	68.30	1M KOH	This work
VN PPC	150.66	178.52	1M KOH	This work
Ni_3N@VN-NF	56	47	1M KOH	[1]
Co/VN	92	54.29	1M KOH	[2]
Mo/VN	108	60	1M KOH	[3]
VN@Ni_3N–Ni/CC	57	40	1M KOH	[4]
Co/N-CNT/VN	63.4	62	1M KOH	[5]
Ru/VN	134	35	0.5 M H_2SO_4	[6]
Ru/VN	144	73	1M KOH	[6]
Co/VN@NC	96	82	1M KOH	[7]
MoS_2/VN	85	53.31	0.5 M H_2SO_4	[8]
VN/Co@NCNT	180	80.9	1M KOH	[9]
VN/Co/P	137	81	1 M KOH	[10]

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