Supporting Information:

Screening of Effective NRR Electrocatalysts among the Si-based MSi_2N_4 (M = Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, and W) Monolayers

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Table S1. Vibrational frequencies, zero point energies and entropy of different adsorption species at 298.15 K on the $TiSi_2N_4$.

Adsorption Species	Vibrational Frequencies (cm^{-1})						E_{ZPE} (eV)	TS (eV)
***N-N**	1363.954	592.946	400.387	295.246	289.073	185.576	0.230	0.038
***N-NH**	3201.160	1312.248	988.396	751.756	621.717	474.223	0.551	0.075
	345.459	317.936	239.098					
***NH-NH**	3293.861	3281.939	1303.369	1271.091	929.295	765.065	0.798	0.104
	683.174	534.238	425.233	321.020	269.057	224.955		
***N-NH_2**	3343.887	3234.774	1576.444	1208.313	1083.594	887.279	0.835	0.101
	485.925	382.437	358.434	328.733	202.469	184.244		
***NH-NH_2**	3429.753	3375.781	3326.654	1609.939	1349.624	1275.536	1.125	0.158
	1126.768	914.628	653.784	525.350	338.496	268.952		
	160.227	119.730	68.321					
***N**	740.812	559.530	490.204				0.115	0.017
***NH**	3168.836	989.956	816.674	583.708	439.831	368.494	0.391	0.033
***NH_2**	3438.404	3333.918	1501.757	702.281	554.504	391.843	0.659	0.093
	255.257	241.165	202.327					
***NH_3**	3466.364	3405.122	3238.110	1600.450	1591.995	1113.152	0.959	0.226
	389.538	272.528	162.142	141.418	58.889	45.035		

Table S2. Lattice parameters of the 2D unit cell and the corresponding 3×3 supercell of the MSi_2N_4 monolayers (in Å).

NO.	Substrate	Lattice constant (Å)	a(Å)	b(Å)
1	$TiSi_2N_4$	2.932	8.796	8.796
2	$HfSi_2N_4$	3.022	9.066	9.066
3	$ZrSi_2N_4$	3.034	9.102	9.102
4	VSi_2N_4	2.883	8.649	8.649
5	$NbSi_2N_4$	2.965	8.895	8.895
6	$TaSi_2N_4$	2.967	8.901	8.901
7	$CrSi_2N_4$	2.844	8.532	8.532
8	$MoSi_2N_4$	2.909	8.727	8.727
9	WSi_2N_4	2.915	8.745	8.745

Table S3. Calculated adsorption free energy (ΔG) of N_2 on different size of the defective $TiSi_2N_4$ periodic supercells. ΔΔG is the energy difference with respect to ΔG on the 3×3 periodic supercell (in eV).

	ΔG	ΔΔG
3×3	-0.42	0
4×4	-0.45	0.03
5×5	-0.36	-0.06

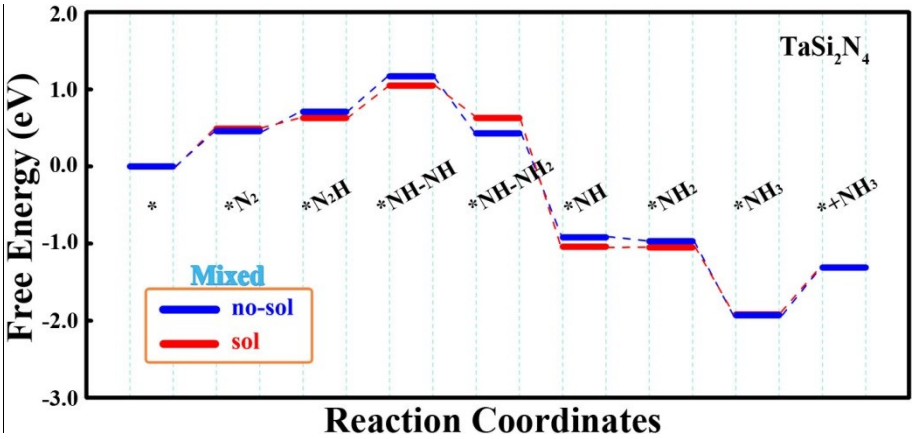

Figure S1. Free energy diagrams of NRR catalyzed by the $TaSi_2N_4$ monolayer along mixed pathway without and with aqueous solvent.

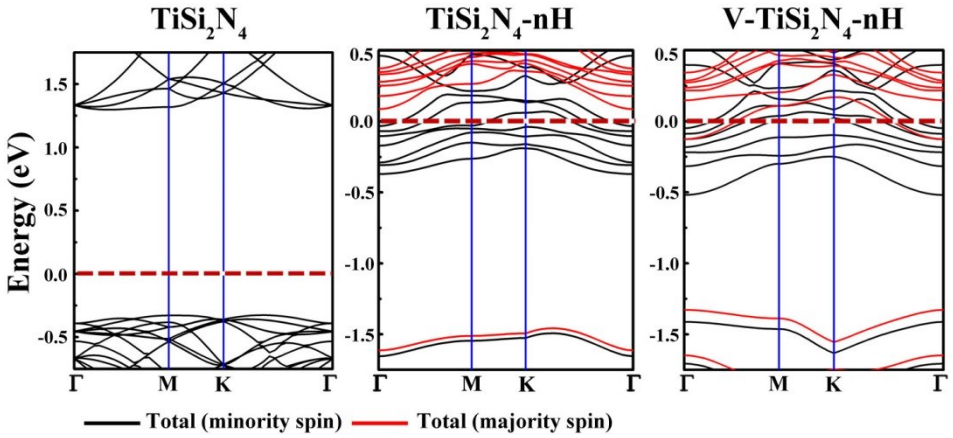

Figure S2. Band structures of $TiSi_2N_4$, $TiSi_2N_4$-nH (pre-hydrogenation) and V-$TiSi_2N_4$-nH (with the N-vacancy). The Fermi level is set to zero.

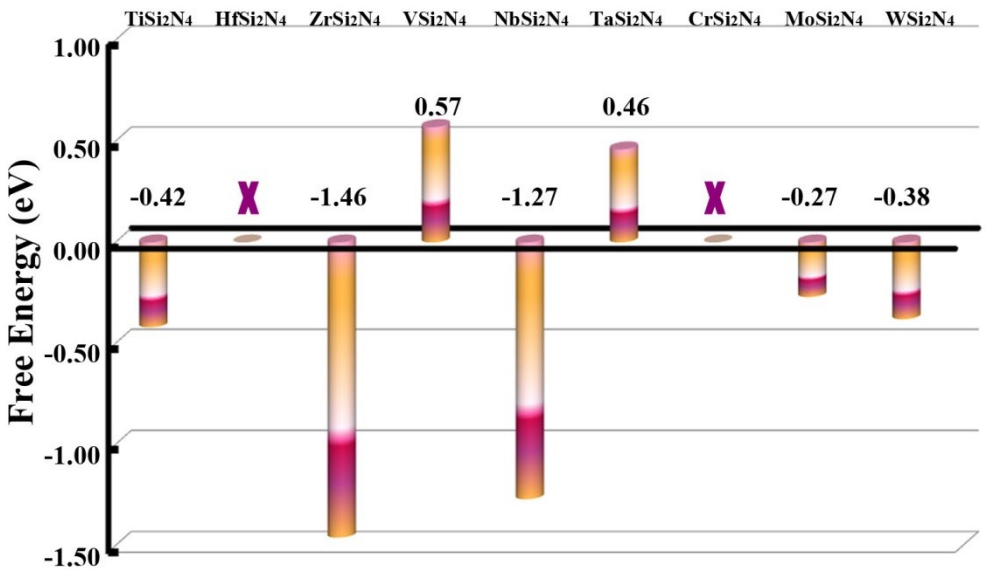

Figure S3. Adsorption free energies of N_2 on 9 kinds of defective MSi_2N_4 materials.

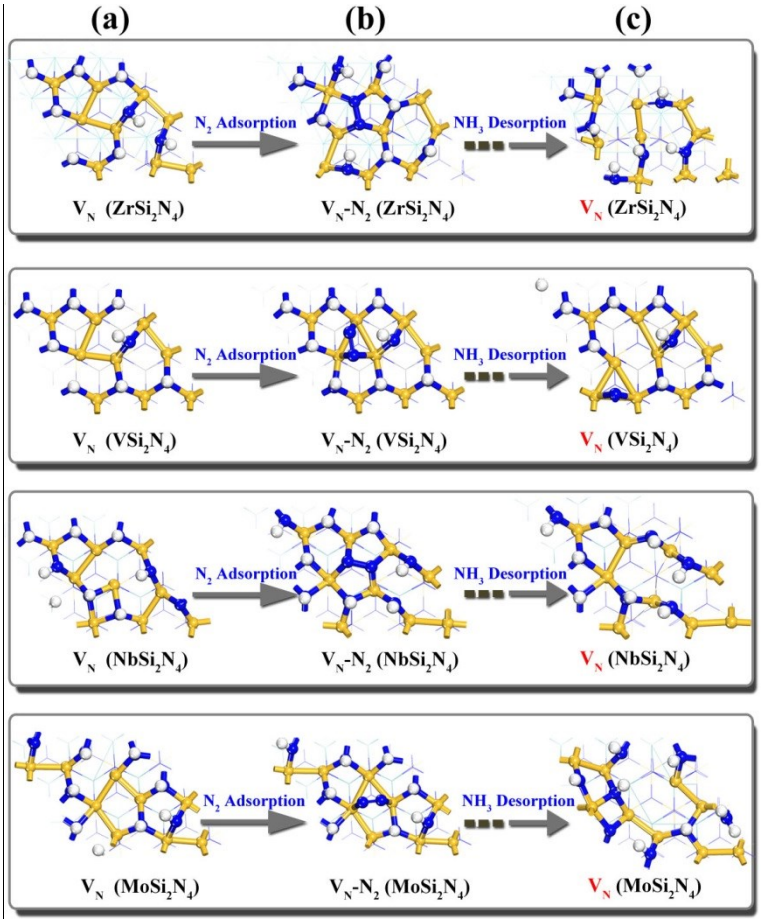

Figure S4. Illustrations of surface reconstruction on the $ZrSi_2N_4$, VSi_2N_4, $NbSi_2N_4$ and $MoSi_2N_4$ monolayers. The observed strong surface reconstruction means that N_2 cannot be captured again after NH_3 desorption.

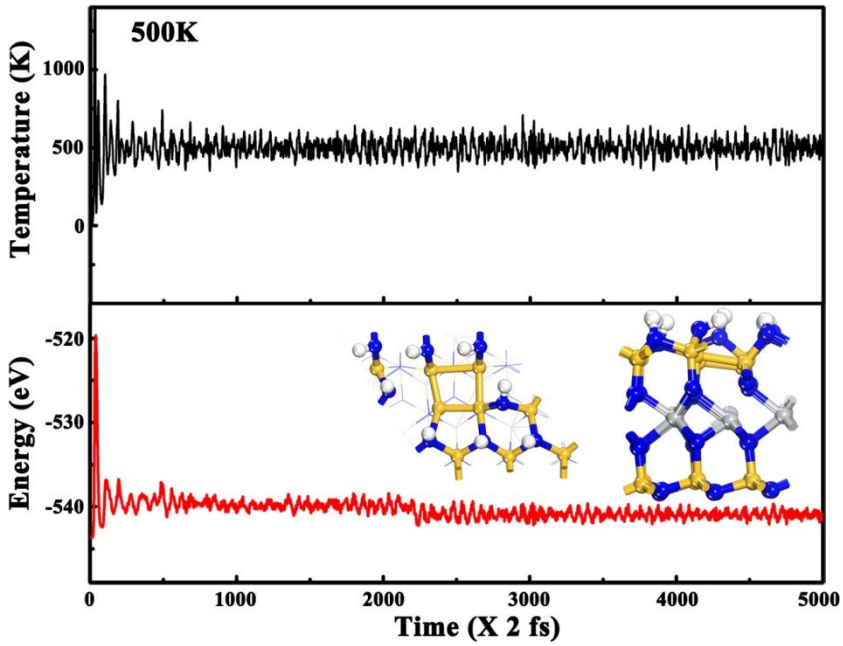

Figure S5. Variations of the temperature and total energy vs time for AIMD simulations of $TiSi_2N_4$. Insets are the top and side views of snapshots at 10 ps.

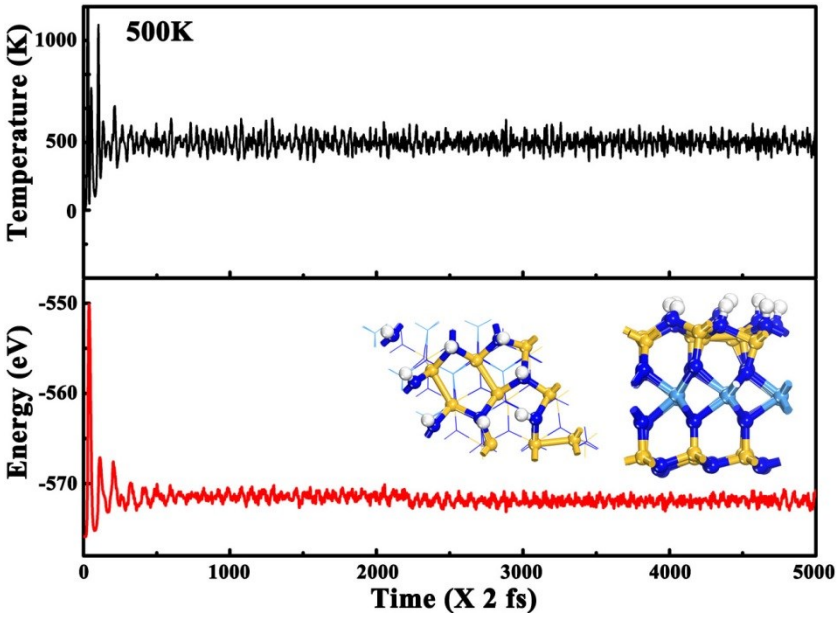

Figure S6. Variations of the temperature and total energy vs time for AIMD simulations of $TaSi_2N_4$. Insets are the top and side views of snapshots at 10 ps.

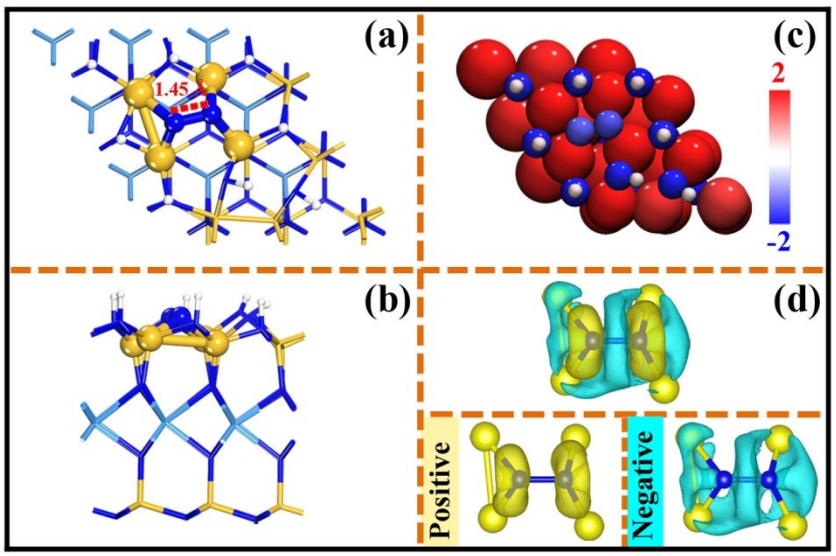

Figure S7. (a) Top and (b) side views of N_2 adsorbed on $TaSi_2N_4$. (c) Atomic charge coloring chart and (d) charge density difference of N_2 on the $TiSi_2N_4$ monolayer. The isosurface value is set to be 0.003 e/Å^3 and the positive and negative charges are shown in yellow and cyan, respectively.

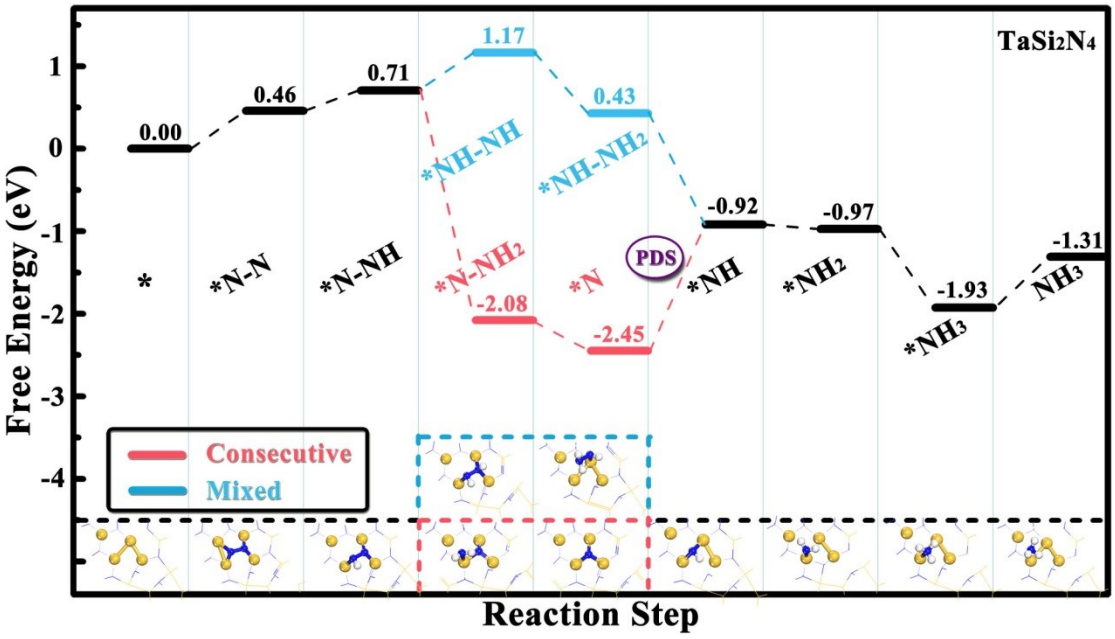

Figure S8. Free energy diagrams for N_2 reduction on $TaSi_2N_4$ through mixed and consecutive mechanisms.

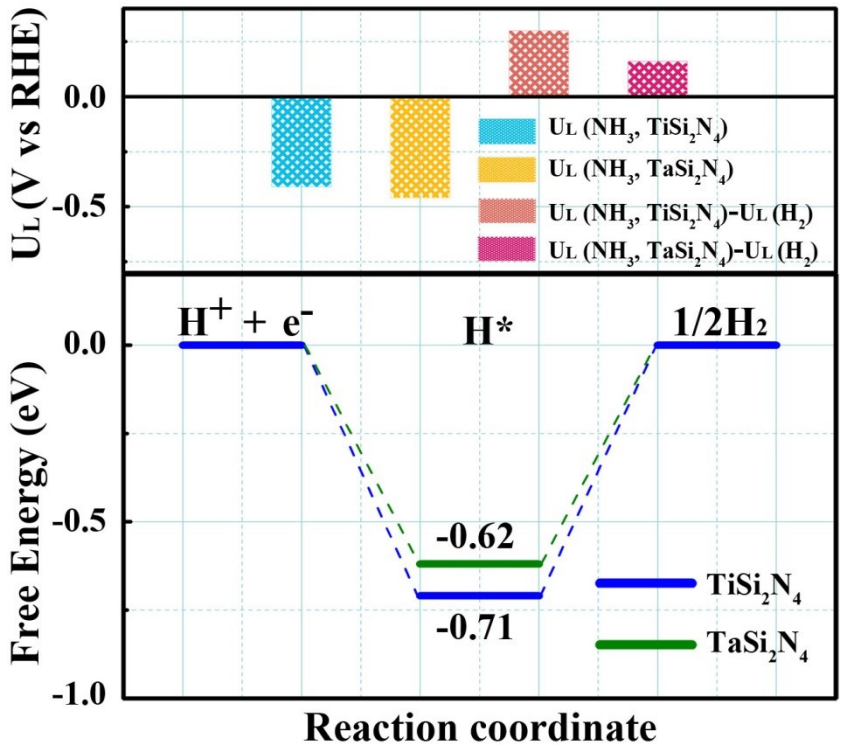

Figure S9. Free energy diagrams for HER on $TiSi_2N_4$ and $TaSi_2N_4$. The limiting potentials for HER $U_L(H_2)$, NRR $U_L(NH_3)$, and the difference between them $U_L(NH_3)$ - $U_L(H_2)$ on two catalysts.