Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.


# Novel two-dimensional Janus $TiSiGeN_4$ monolayer with N vacancies for efficient photocatalytic nitrogen reduction

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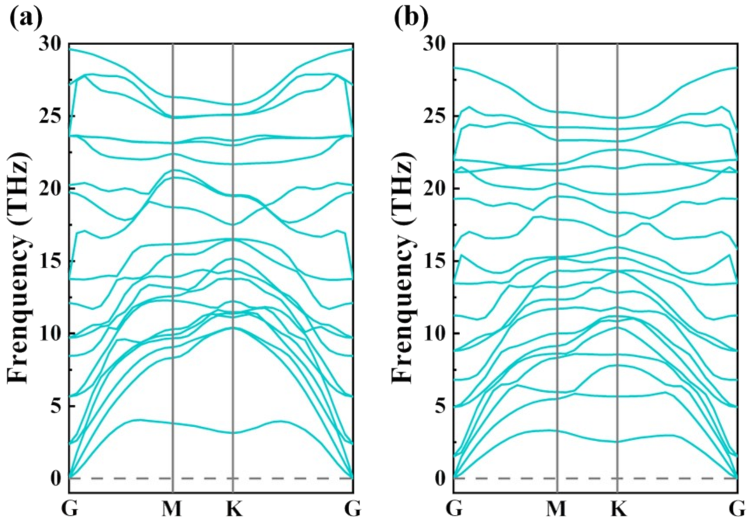


**Fig. S1** Phonon dispersion curves for (a) $TiSi_2N_4$ and (b) $TiSiGeN_4$.

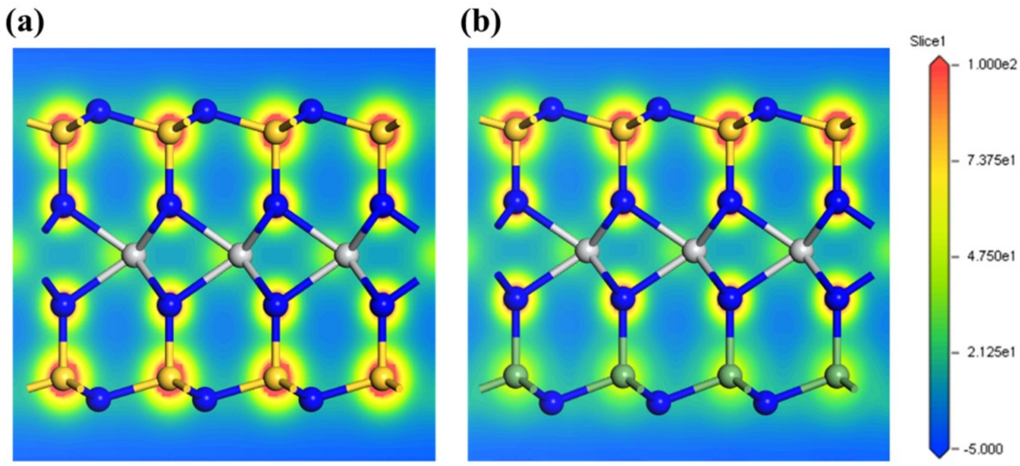


**Fig. S2** Profile of electrostatic potential of (a) $TiSi_2N_4$ and (b) $TiSiGeN_4$. The different colors in the picture represent different electron densities, as shown in the scale on the right.

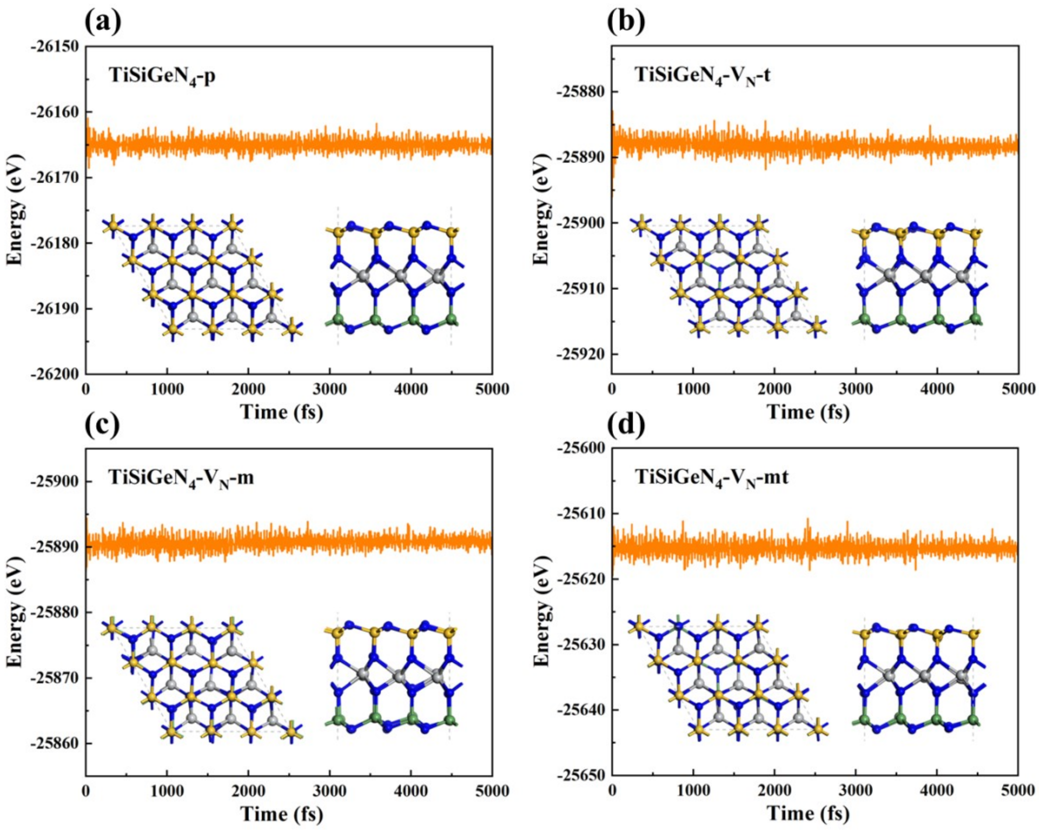


**Fig. S3** Variations of the total energy versus time for AIMD simulations of Janus $TiSiGeN_4$ with different N vacancies. The AIMD runs under 500 K for 5 ps with a time step of 1 fs.

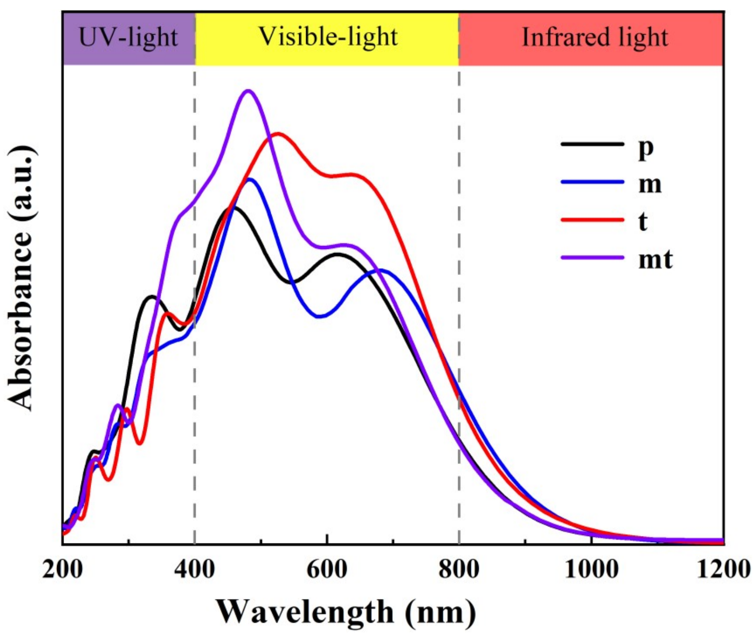


**Fig. S4** Optical absorption spectra of $TiSiGeN_4$-p, $TiSiGeN_4$-$V_N$-t, $TiSiGeN_4$-$V_N$-m, and $TiSiGeN_4$-$V_N$-mt.

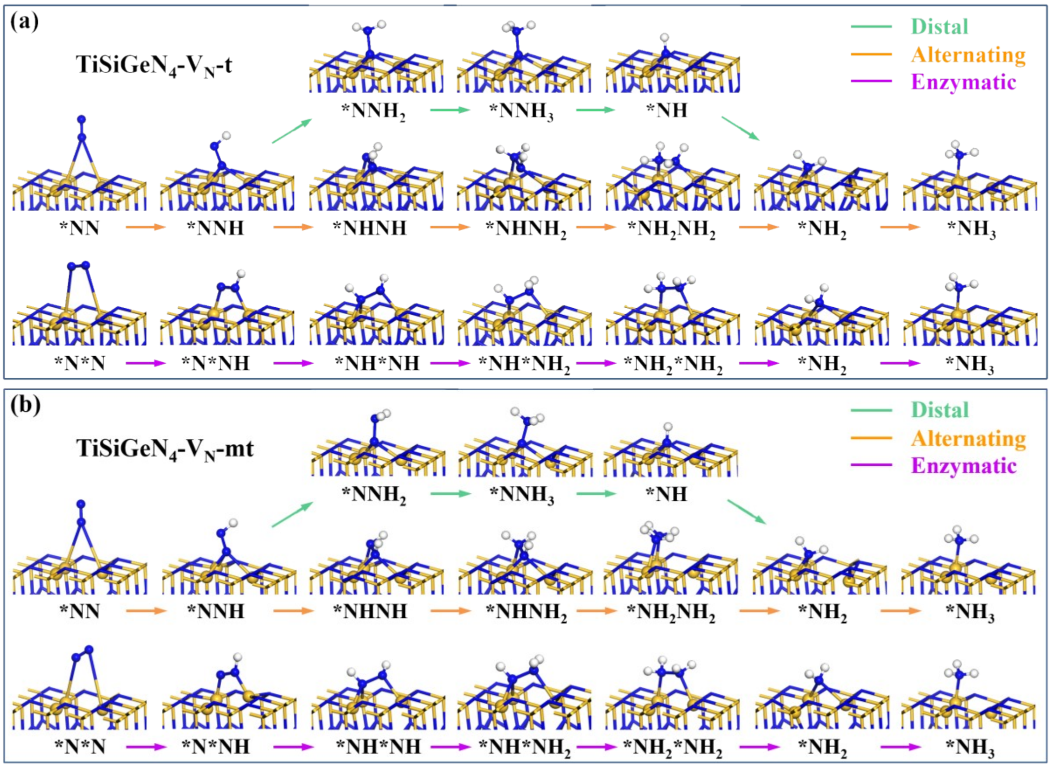


**Fig. S5** Optimized structures of various intermediates along the reaction paths of the NRR proceeding on the (a) $TiSiGeN_4$-$V_N$-t and (b) $TiSiGeN_4$-$V_N$-mt surfaces through distal, alternating and enzymatic pathways.

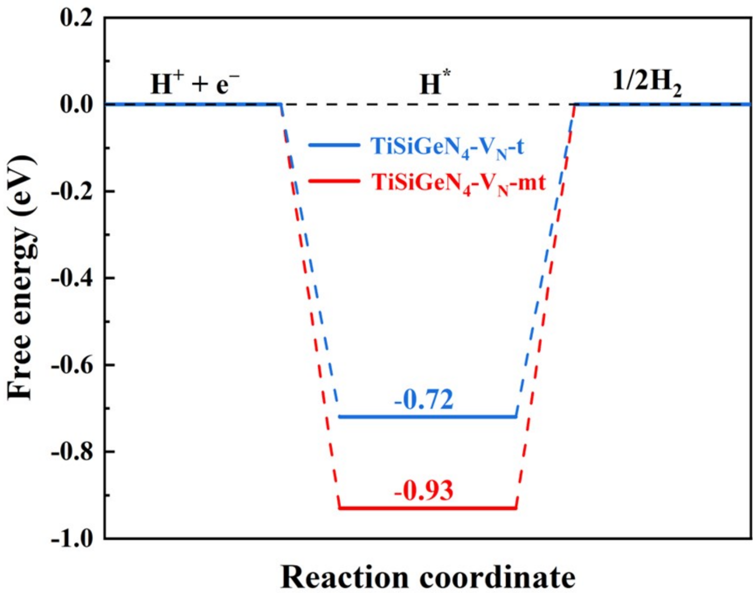


Fig. S6 Free energy diagrams for HER on $TiSiGeN_4$-$V_N$-t and $TiSiGeN_4$-$V_N$-mt.

**Table S1** Free energy corrections: $E_{ZPE}$ and S represent the zero-point energy change and the entropy change of intermediate for NRR on $TiSiGeN_4$-$V_N$-t, where * denoted the adsorption site.

| Species | $E_{ZPE}$ (eV) | *TS* (eV) | $E_{ZPE} - TS$ (eV) |
|---|---|---|---|
| *NN | 0.23 | 0.08 | 0.15 |
| *NNH | 0.55 | 0.09 | 0.46 |
| $*NNH_2$ | 0.84 | 0.11 | 0.73 |
| $*NNH_3$ | 1.01 | 0.13 | 0.88 |
| *NH | 0.41 | 0.03 | 0.38 |
| $*NH_2$ | 0.69 | 0.09 | 0.60 |
| $*NH_3$ | 0.96 | 0.12 | 0.84 |
| *NHNH | 0.80 | 0.11 | 0.69 |
| $*NHNH_2$ | 0.99 | 0.14 | 0.85 |
| $*NH_2NH_2$ | 1.27 | 0.16 | 1.11 |
| *N*N | 0.21 | 0.06 | 0.15 |
| *N*NH | 0.53 | 0.08 | 0.45 |
| *NH*NH | 0.79 | 0.10 | 0.69 |
| $*NH*NH_2$ | 0.91 | 0.16 | 0.75 |
| $*NH_2*NH_2$ | 1.24 | 0.18 | 1.06 |
| $*NH_2$ | 0.68 | 0.08 | 0.60 |
| $*NH_3$ | 0.96 | 0.12 | 0.84 |
| *H | 0.18 | 0.16 | 0.02 |
| $H_2$ | 0.27 | 0.41 | −0.14 |
| $N_2$ | 0.15 | 0.60 | −0.45 |

| | | | |
|---|---|---|---|
| **$NH_3$** | 0.94 | 0.60 | 0.34 |

**Table S2.** Free energy corrections: $E_{ZPE}$ and S represent the zero-point energy change and the entropy change of intermediate for NRR on $TiSiGeN_4$-$V_N$-mt, where * denoted the adsorption site.

| Species | $E_{ZPE}$ (eV) | $TS$ (eV) | $E_{ZPE} - TS$ (eV) |
|---|---|---|---|
| ***NN** | 0.25 | 0.10 | 0.15 |
| ***NNH** | 0.57 | 0.10 | 0.47 |
| **$*NNH_2$** | 0.86 | 0.11 | 0.75 |
| **$*NNH_3$** | 1.09 | 0.12 | 0.97 |
| ***NH** | 0.45 | 0.03 | 0.42 |
| **$*NH_2$** | 0.69 | 0.09 | 0.60 |
| **$*NH_3$** | 0.92 | 0.16 | 0.76 |
| ***NHNH** | 0.82 | 0.09 | 0.73 |
| **$*NHNH_2$** | 1.00 | 0.14 | 0.86 |
| **$*NH_2NH_2$** | 1.30 | 0.18 | 1.12 |
| ***N*N** | 0.28 | 0.04 | 0.15 |
| ***N*NH** | 0.56 | 0.04 | 0.45 |
| ***NH*NH** | 0.84 | 0.06 | 0.78 |
| **$*NH*NH_2$** | 0.99 | 0.10 | 0.89 |
| **$*NH_2*NH_2$** | 1.25 | 0.17 | 1.08 |
| **$*NH_2$** | 0.70 | 0.09 | 0.61 |
| **$*NH_3$** | 0.93 | 0.17 | 0.76 |
| ***H** | 0.18 | 0.17 | 0.01 |

| | | | |
|---|---|---|---|
| **$H_2$** | 0.27 | 0.41 | −0.14 |
| **$N_2$** | 0.15 | 0.60 | −0.45 |
| **$NH_3$** | 0.94 | 0.60 | 0.34 |