Supporting Information

Defective Fe_3GeTe_2 Monolayer as a Promissing Electrocatalyst for Spontaneous Nitrogen Reduction Reaction

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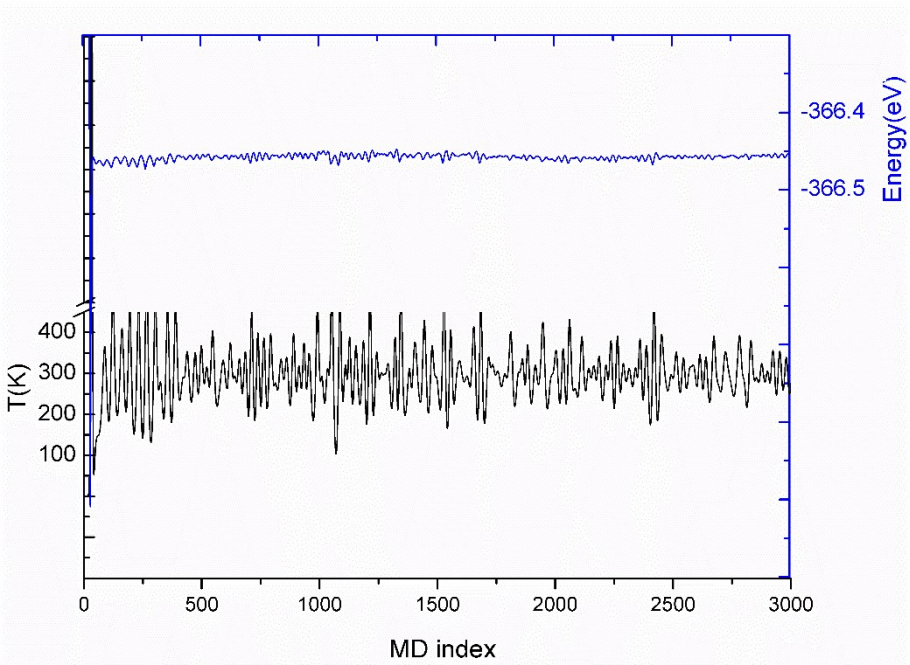

Fig. S1 The temperature and energy against the MD simulation time.

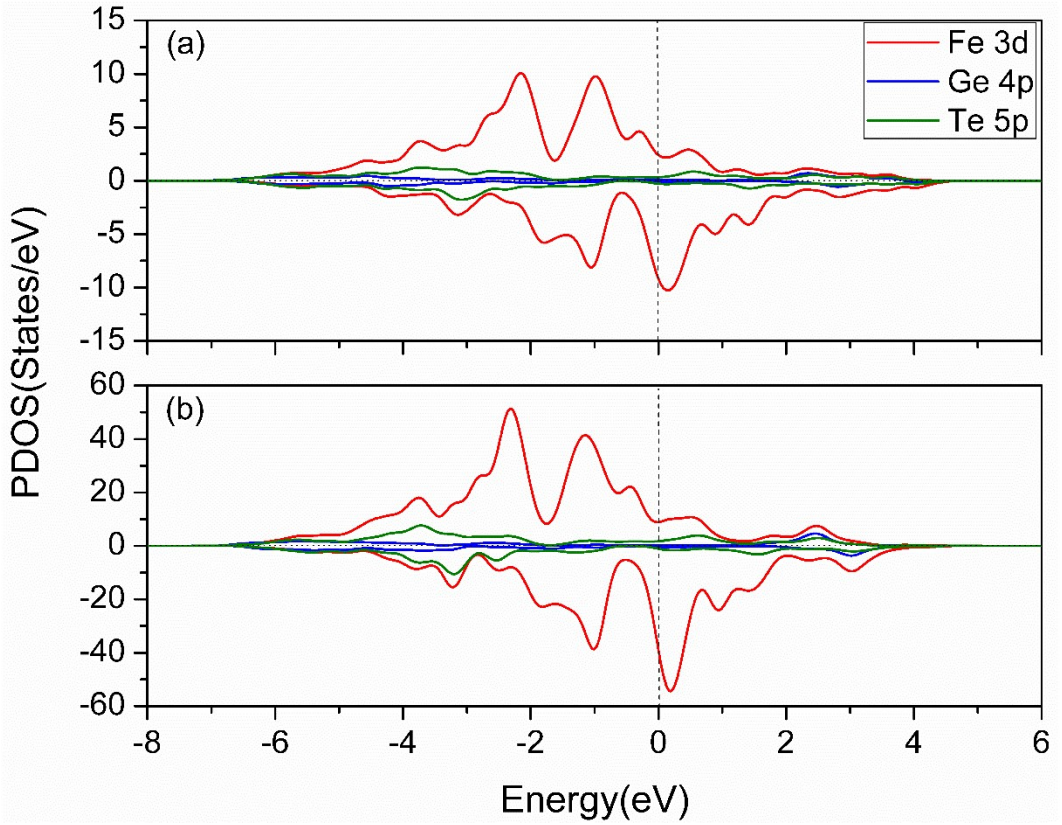

Fig. S2 Spin-polarized PDOS for the bulk Fe_3GeTe_2 (a) and pristine Fe_3GeTe_2 monolayer (b).

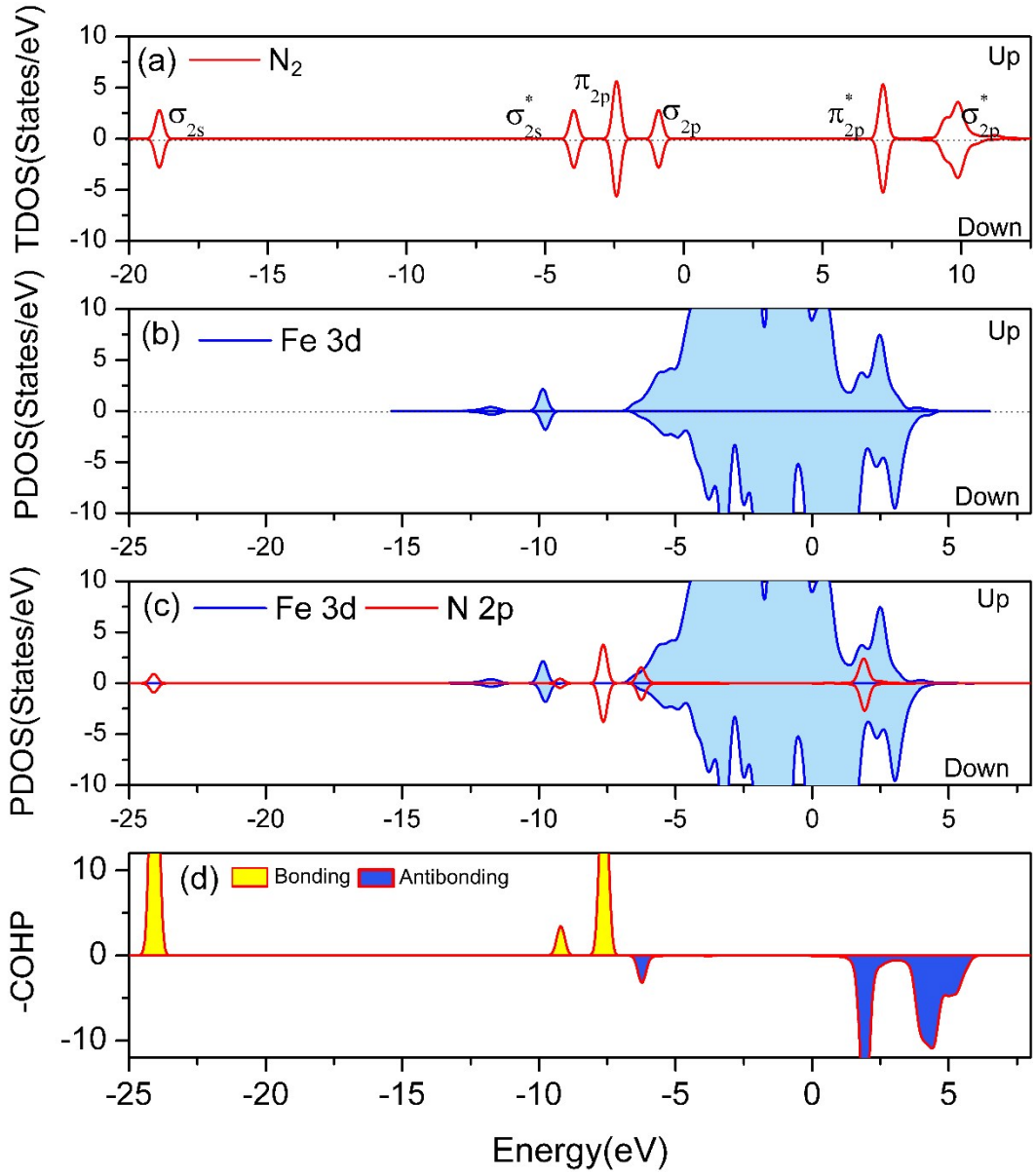

Fig. S3 Molecular orbitals for free N_2 (a). Projected density of states of Fe 3*d* orbitals of pristine Fe_3GeTe_2 monolayer (b), and the Fe 3*d* and N 2*p* orbitals of N_2 adsorbed pristine Fe_3GeTe_2 (c). The crystal orbital Hamilton population of N_2 on the pristine Fe_3GeTe_2 surface(d). The bonding and antibonding states in -COHP are depicted by yellow and blue, respectively.

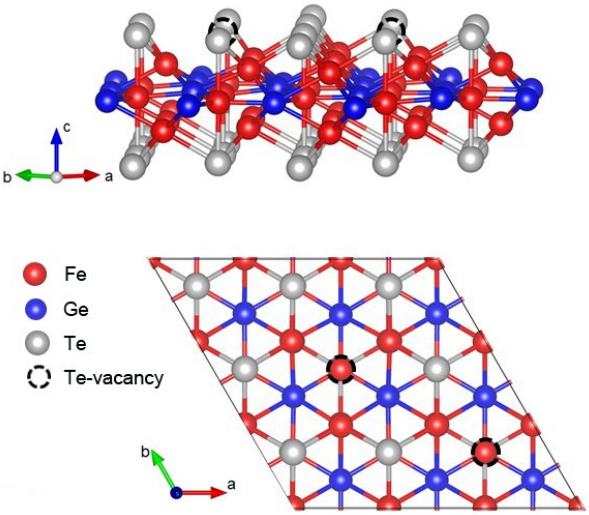

Fig. S4 The side and top views of the defective Fe_3GeTe_2 with double-Te vacancies.

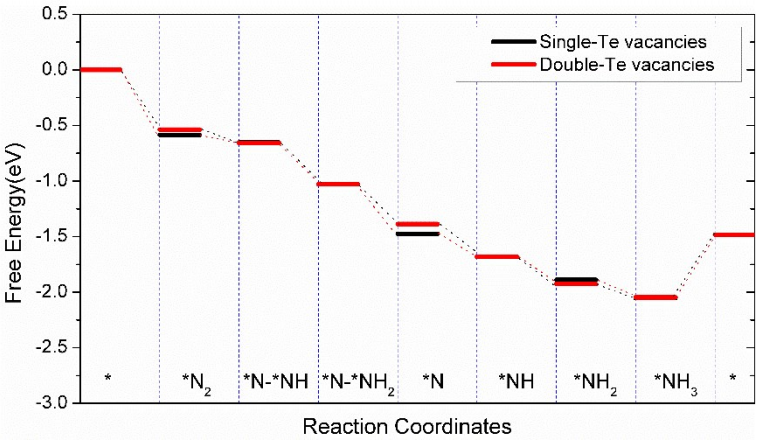

Fig. S5 The NRR pathway on defect Fe_3GeTe_2 monolayer with single- and double-Te vacancies.

Table S1. The formation energy of cation vacancy (Fe or Ge vacancy) and anion vacancy (Te vacancy) in Fe_3GeTe_2 calculated by the following formula: $E_f = E_{defective} - E_{pure} + \mu_{vacancy}$, where $E_{defective}$ and E_{pure} are the total energies of the defective Fe_3GeTe_2 with one vacancy in a unit cell, and the pristine Fe_3GeTe_2, respectively. $\mu_{vacancy}$ is the chemical potential of the Fe, Ge or Te atoms.

	Fe_I	Ge	Te
E_f(eV)	6.707	8.268	2.424

Table S2. The partial and integrated local magnetic moments in pristine and defective Fe_3GeTe_2 monolayer in units of μ_B.

	Pristine Fe_3GeTe_2				Defective Fe_3GeTe_2			
	s	p	d	tot	s	p	d	tot
Ge1	-0.003	-0.06	0.01	-0.053	-0.002	-0.064	0.01	-0.056
Ge2	-0.003	-0.06	0.01	-0.053	-0.003	-0.063	0.01	-0.055
Ge3	-0.003	-0.06	0.01	-0.053	-0.002	-0.063	0.01	-0.055
Ge4	-0.003	-0.06	0.01	-0.053	-0.003	-0.062	0.011	-0.054
Ge5	-0.003	-0.06	0.01	-0.053	-0.004	-0.063	0.011	-0.057
Ge6	-0.003	-0.06	0.01	-0.053	-0.002	-0.063	0.01	-0.055
Ge7	-0.003	-0.06	0.01	-0.053	-0.002	-0.064	0.01	-0.055
Ge8	-0.003	-0.06	0.01	-0.053	-0.004	-0.063	0.011	-0.056
Ge9	-0.003	-0.06	0.01	-0.053	-0.002	-0.063	0.01	-0.056
Fe1	0.006	0.026	1.812	1.843	0.006	0.025	1.806	1.837
Fe2	0.006	0.026	1.811	1.843	0.005	0.025	1.873	1.903
Fe3	-0.002	0.002	0.992	0.993	-0.002	0.001	1.04	1.039
Fe4	0.006	0.026	1.812	1.844	0.006	0.024	1.808	1.838
Fe5	0.006	0.026	1.811	1.843	0.006	0.025	1.883	1.915
Fe6	-0.002	0.002	0.992	0.993	-0.002	0.001	1.021	1.02
Fe7	0.006	0.026	1.812	1.844	0.006	0.027	1.92	1.953
Fe8	0.006	0.026	1.812	1.843	0.006	0.025	1.797	1.828
Fe9	-0.002	0.002	0.992	0.993	-0.002	0.002	0.993	0.993
Fe10	0.006	0.026	1.812	1.844	0.006	0.027	1.913	1.945
Fe11	0.006	0.026	1.812	1.843	0.006	0.026	1.795	1.827
Fe12	-0.002	0.002	0.992	0.993	-0.002	0.001	1.037	1.037
Fe13	0.006	0.026	1.812	1.844	0.006	0.028	1.961	1.995
Fe14	0.006	0.026	1.812	1.843	0.009	0.029	2.075	2.114
Fe15	-0.002	0.002	0.992	0.993	0	-0.001	1.369	1.368
Fe16	0.006	0.026	1.813	1.844	0.006	0.027	1.922	1.955
Fe17	0.006	0.026	1.812	1.843	0.006	0.025	1.796	1.827
Fe18	-0.002	0.002	0.992	0.993	-0.002	0.001	1.029	1.029
Fe19	0.006	0.026	1.812	1.844	0.006	0.025	1.805	1.836

Fe20	0.006	0.026	1.811	1.843	0.005	0.025	1.875	1.906
Fe21	-0.002	0.002	0.992	0.992	-0.001	0.003	0.966	0.967
Fe22	0.006	0.026	1.812	1.844	0.006	0.028	1.965	1.999
Fe23	0.006	0.026	1.812	1.843	0.01	0.029	2.074	2.114
Fe24	-0.002	0.002	0.992	0.993	-0.002	0.001	1.025	1.024
Fe25	0.006	0.026	1.812	1.844	0.006	0.028	1.959	1.993
Fe26	0.006	0.026	1.812	1.843	0.008	0.028	2.078	2.114
Fe27	-0.002	0.002	0.992	0.993	-0.002	0.001	1.036	1.035
Te1	0.004	-0.039	0.003	-0.031	0.005	-0.042	0.003	-0.034
Te2	0.004	-0.039	0.003	-0.031	0.003	-0.043	0.003	-0.036
Te3	0.004	-0.039	0.003	-0.031	0.005	-0.043	0.003	-0.035
Te4	0.004	-0.039	0.003	-0.031	0.004	-0.033	0.003	-0.026
Te5	0.004	-0.039	0.003	-0.031	0.005	-0.04	0.003	-0.032
Te6	0.004	-0.039	0.003	-0.031	0.004	-0.037	0.003	-0.03
Te7	0.004	-0.039	0.003	-0.031	0.005	-0.043	0.003	-0.035
Te8	0.004	-0.039	0.003	-0.031	0.004	-0.04	0.003	-0.033
Te9	0.004	-0.039	0.003	-0.031	0.005	-0.04	0.004	-0.031
Te10	0.004	-0.039	0.003	-0.031				
Te11	0.004	-0.039	0.003	-0.031	0.005	-0.042	0.003	-0.035
Te12	0.004	-0.039	0.003	-0.031	0.004	-0.04	0.003	-0.034
Te13	0.004	-0.039	0.003	-0.031	0.005	-0.04	0.003	-0.033
Te14	0.004	-0.039	0.003	-0.031	0.005	-0.036	0.003	-0.029
Te15	0.004	-0.039	0.003	-0.031	0.005	-0.043	0.003	-0.035
Te16	0.004	-0.039	0.003	-0.031	0.004	-0.033	0.003	-0.025
Te17	0.004	-0.039	0.003	-0.031	0.005	-0.041	0.003	-0.034
Te18	0.004	-0.039	0.003	-0.031	0.003	-0.043	0.003	-0.037