Electronic Supplementary Information (ESI)

Single Atom Doped Arsenene as Elecocatalysts for Reducing Nitrogen to Ammonia: A DFT Study

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Table S1 The average bond lengths of metal-As.

Metal (m)	$d_{m\text{-}As}$ (Å)
V	2.47
Cr	2.46
Fe	2.39
Co	2.27
Cu	2.37
Ru	2.36
Pd	2.44
Ag	2.54
Pt	2.41
Au	2.49

Table S2 The band gap values (DFT-PBE level) of TM doped arsenene.

TM/Ars	Band gap value (eV)
V/Ars	~ 0.00
Cr/Ars	0.78
Fe/Ars	~ 0.00
Co/Ars	0.66
Cu/Ars	~ 0.00
Ru/Ars	0.25
Pd/Ars	~ 0.00
Ag/Ars	~ 0.00
Pt/Ars	~ 0.00
Au/Ars	~ 0.00

Table S3 The Gibbs free energies change of N_2 adsorption with the most favorable manner, and the distant of N-N bond. Bader charge for TM-doped system and N_2 molecule.

Metal (m)	$d_{N\text{-}N}$ (Å)	$Q_{system-N_2}$ (e)
V	1.13	0.32
Cr	1.12	0.21
Fe	1.14	0.35
Co	1.13	0.20
Ru	1.13	0.28

Table S4 The comparable results of this work and the others NRR catalysts.

Catalysts	U_{oneset} (V)	Refs.
V/Ars	-0.26	In this work
B-B_lP and B-B_bP	-0.78 and -0.92	[1]
Ru/ Boron	-0.42	[2]
Ru_1@C_2N, Ru_1@T-C_3N_4, and Ru_1@γ-graphynes	-0.94, -0.96 and -0.98	[3]
W@g-C_3N_4	-0.35	[4]
Mo@C_2N	-0.17	[5]
V@β_{12}-Boron	-0.28	[6]
B/g-C_3N_4	-0.20	[7]

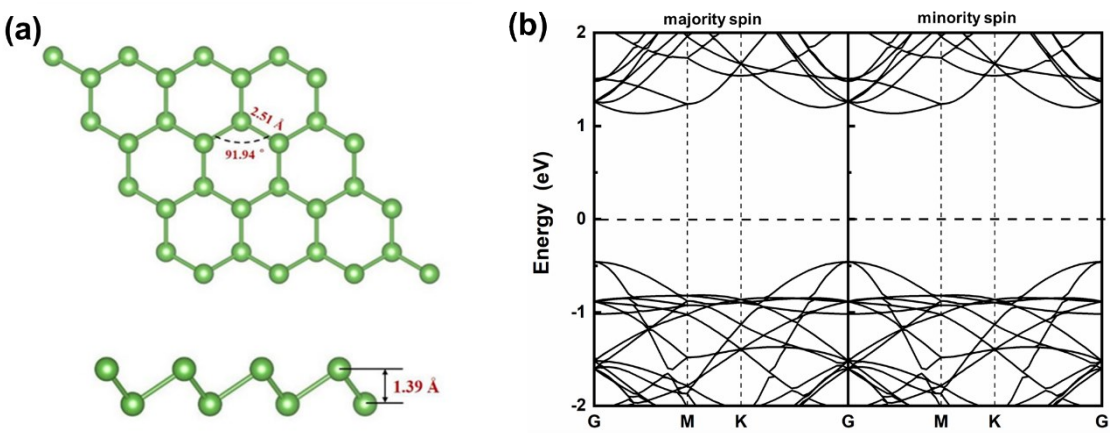

Fig. S1 The pristine arsenene nanosheet of (a) top view and side view, and (b) the corresponding band structure (DFT-PBE level). The Fermi-level is set to be zero denoted by dash line. The green color is represented for arsenic atom.

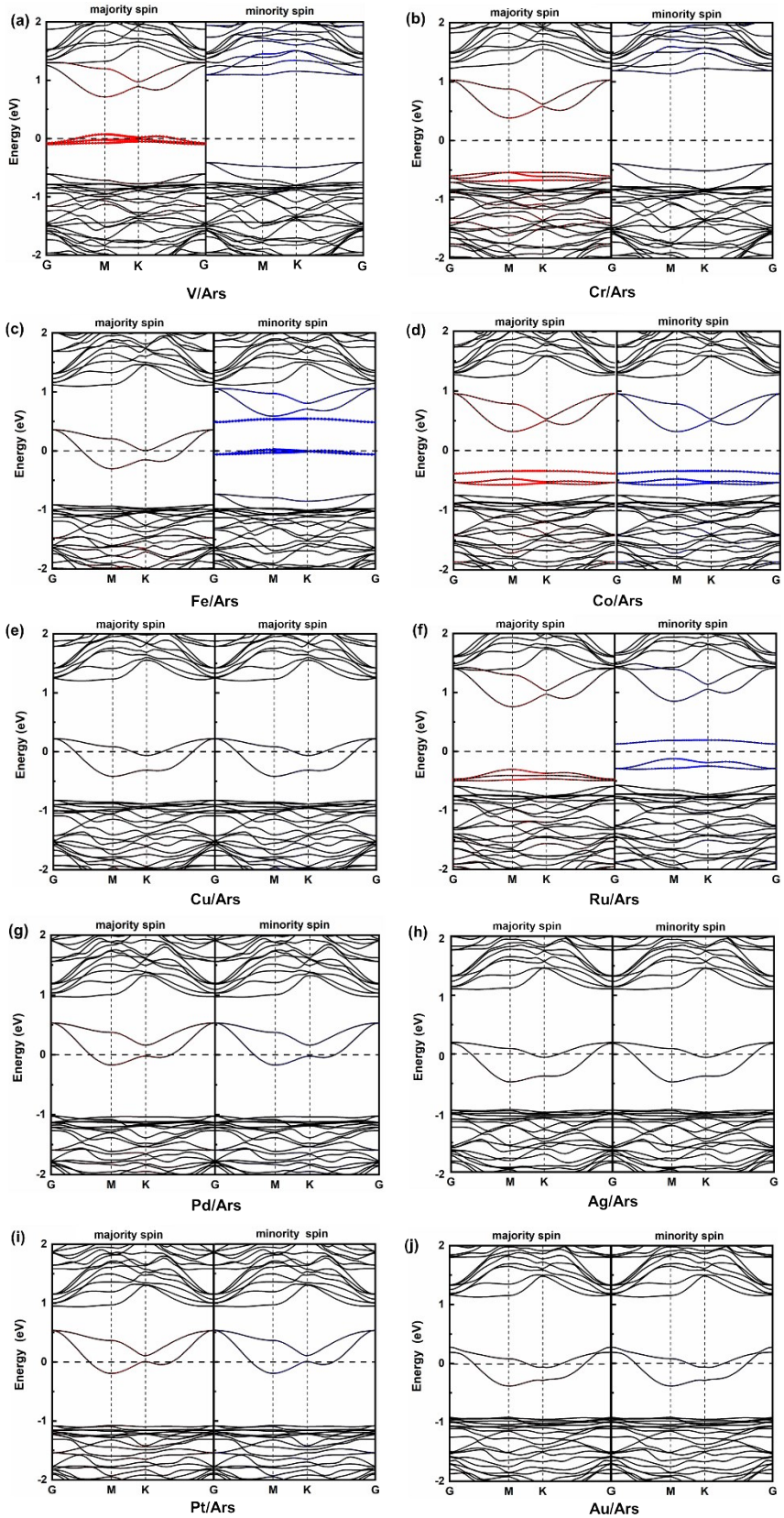

Fig. S2 Electronic band structures (DFT-PBE level) of TM atoms (i.e., V, Cr, Fe, Co, Cu, Ru, Pd, Ag, Pt and Au) doped arsenene. The Fermi-level is indicated by the dash line, and red and blue spots represents TM contributions from majority and minority spins.

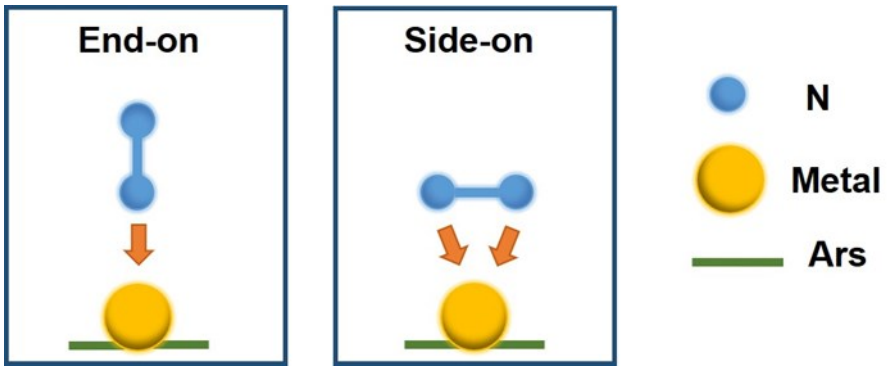

Fig. S3 The N_2 adsorption on TM/Ars with end-on and side-on configurations.

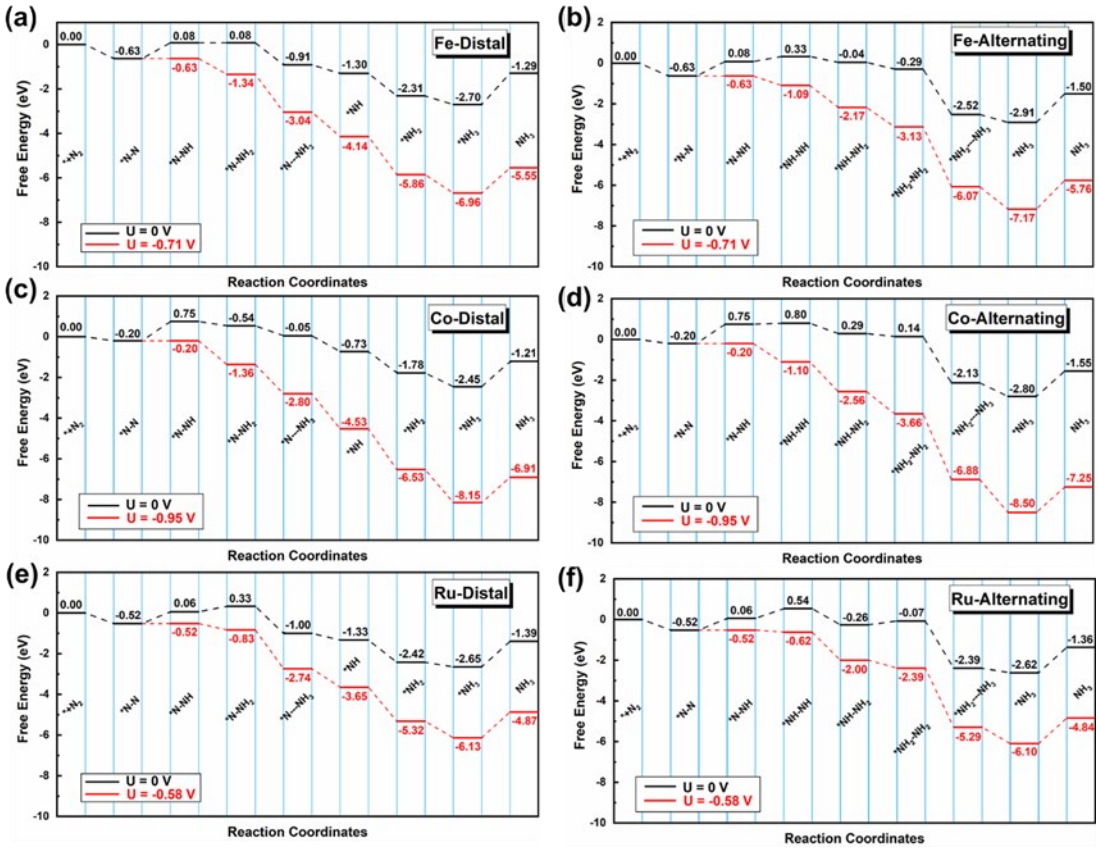

Fig. S4 Free energies profiles for Fe-, Co-, Ru-doped arsenene nanosheet via distal ways (i.e., (a) (c) (e)) and alternating ways (i.e., (b) (d) (f)).

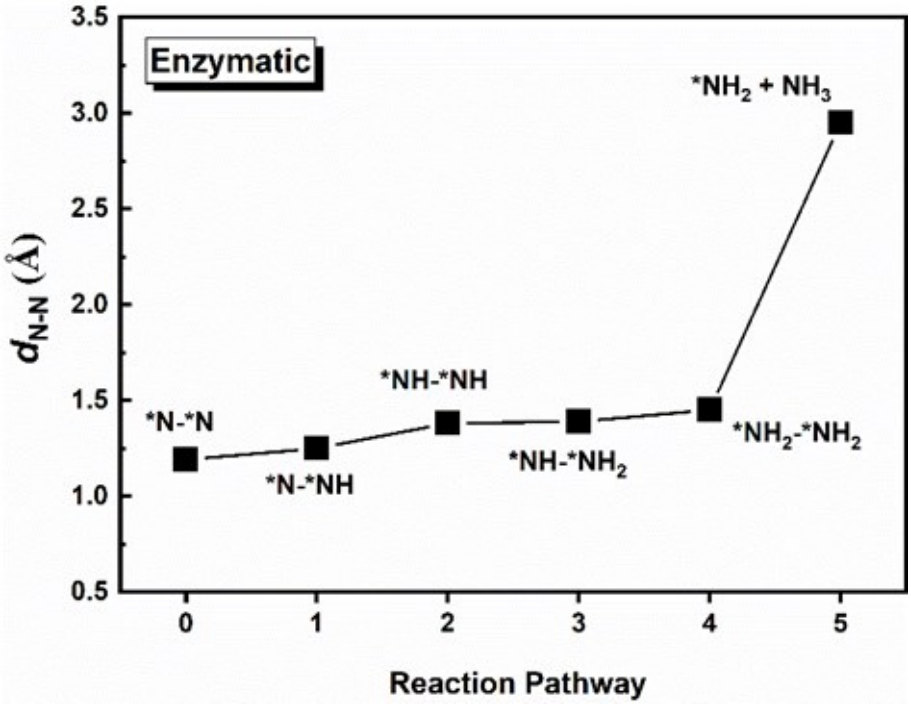

Fig. S5 The variation of the N≡N bond length (d_{N-N}) via the enzymatic pathway on V/Ars electrocatalyst for NRR process.

Reference

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