Efficient Urea Formation from N_2O+CO on Dual-Atom Catalysts TM_2/*g*-CN

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Table S1 Elementary reactions for the considered pathways for $N_2O \rightarrow NH_3$ process.

Enzymatic	Consecutive
N_2O (g) + * $\rightarrow$ *N_2O	N_2O (g) + * $\rightarrow$ *N_2O
*N_2O + H^+ + e^- $\rightarrow$ *NNOH	*N_2O + H^+ + e^- $\rightarrow$ *NNOH
*NNOH + H^+ + e^- $\rightarrow$ *NN + H_2O (g)	*NNOH + H^+ + e^- $\rightarrow$ *NN + H_2O (g)
*NN + H^+ + e^- $\rightarrow$ *NNH	*NN + H^+ + e^- $\rightarrow$ *NNH
*NNH + H^+ + e^- $\rightarrow$ *NHNH	*NNH + H^+ + e^- $\rightarrow$ *NNH_2
*NHNH + H^+ + e^- $\rightarrow$ *$NHNH_2$	*NNH_2 + H^+ + e^- $\rightarrow$ *N + NH_3 (g)
*$NHNH_2$ + H^+ + e^- $\rightarrow$ *NH_2NH_2	*N + H^+ + e^- $\rightarrow$ *NH
*NH_2NH_2 + H^+ + e^- $\rightarrow$ *NH_2 + NH_3(g)	*NH + H^+ + e^- $\rightarrow$ *NH_2
*NH_2 + H^+ + e^- $\rightarrow$ *NH_3	*NH_2 + H^+ + e^- $\rightarrow$ *NH_3
*NH_3 $\rightarrow$ * + NH_3 (g)	*NH_3 $\rightarrow$ * + NH_3 (g)

Mixed 1	Mixed 2
N_2O (g) + * $\rightarrow$ *N_2O	N_2O (g) + * $\rightarrow$ *N_2O
*N_2O + H^+ + e^- $\rightarrow$ *NNOH	*N_2O + H^+ + e^- $\rightarrow$ *NNOH
*NNOH + H^+ + e^- $\rightarrow$ *NN + H_2O (g)	*NNOH + H^+ + e^- $\rightarrow$ *NN + H_2O (g)
*NN + H^+ + e^- $\rightarrow$ *NNH	*NN + H^+ + e^- $\rightarrow$ *NNH
*NNH + H^+ + e^- $\rightarrow$ *NNH_2	*NNH + H^+ + e^- $\rightarrow$ *NHNH
*NNH_2 + H^+ + e^- $\rightarrow$ *$NHNH_2$	*NHNH + H^+ + e^- $\rightarrow$ *$NHNH_2$
*$NHNH_2$ + H^+ + e^- $\rightarrow$ *NH_2NH_2	*$NHNH_2$ + H^+ + e^- $\rightarrow$ *NH + NH_3 (g)
*NH_2NH_2 + H^+ + e^- $\rightarrow$ *NH_2 + NH_3(g)	*NH + H^+ + e^- $\rightarrow$ *NH_2
*NH_2 + H^+ + e^- $\rightarrow$ *NH_3	*NH_2 + H^+ + e^- $\rightarrow$ *NH_3
*NH_3 $\rightarrow$ * + NH_3 (g)	*NH_3 $\rightarrow$ * + NH_3 (g)

Table S2 Calculated binding energy (E_b) of transition metal (TM) atoms on g-CN and cohesive energy (E_{coh}) of TM atoms. E_b is calculated by $E_b = (E_{DACs} - E_{g\text{-}CN} - 2E_M)/2$, where E_{DACs}, $E_{g\text{-}CN}$ and E_M are the energies of DACs, pure g-CN and metal atoms, respectively. E_{coh} is looked up in the KnowledgeDoor database.

TM_2/g-CN	E_b (eV)	E_{coh} (eV)	TM_2/g-CN	E_b (eV)	E_{coh} (eV)
Ti_2/g-CN	–6.34	–4.85	Rh_2/g-CN	–5.39	–5.75
V_2/g-CN	–6.08	–5.31	Pd_2/g-CN	–3.41	–3.89
Cr_2/g-CN	–4.21	–4.1	Ag_2/g-CN	–1.75	–2.95
Mn_2/g-CN	–3.49	–2.92	Cd_2/g-CN	–0.79	–1.16
Fe_2/g-CN	–4.41	–4.28	Hf_2/g-CN	–6.26	–6.44
Co_2/g-CN	–4.62	–4.39	Ta_2/g-CN	–8.12	–8.10
Ni_2/g-CN	–4.92	–4.44	W_2/g-CN	–9.01	–8.90
Cu_2/g-CN	–2.99	–3.49	Re_2/g-CN	–9.07	–8.03
Zn_2/g-CN	–1.46	–1.35	Os_2/g-CN	–6.88	–8.17
Zr_2/g-CN	–6.22	–6.25	Ir_2/g-CN	–6.39	–6.94

Nb$_2$/g-CN	–6.86	–7.57	Pt$_2$/g-CN	–5.36	–5.84
Mo$_2$/g-CN	–6.18	–6.82	Au$_2$/g-CN	–1.80	–3.81
Ru$_2$/g-CN	–6.91	–6.74			

Table S3 Free energy change of adsorbed NCON ($\Delta G_{*\text{NCON}}$) on TM$_2$/g-CN and transferred charge from TM$_2$/g-CN to adsorbed NCON.

TM$_2$/g-CN	$\Delta G_{*\text{NCON}}$ (eV)	Charge (e^-)
Ti$_2$/g-CN	–4.04	1.64
Cr$_2$/g-CN	–2.29	1.23
Mn$_2$/g-CN	–2.64	1.18
Fe$_2$/g-CN	–2.02	1.10
Co$_2$/g-CN	–1.99	1.20
W$_2$/g-CN	–4.96	1.41
Re$_2$/g-CN	–3.87	1.27

Table S4 Free energy change of adsorbed NCOHN ($\Delta G_{*\text{NCOHN}}$) and NCONH ($\Delta G_{*\text{NCONH}}$) on TM$_2$/g-CN. The unit is eV.

TM$_2$/g-CN	$\Delta G_{*\text{NCOHN}}$	$\Delta G_{*\text{NCONH}}$
Ti$_2$/g-CN	–4.27	–4.95
Cr$_2$/g-CN	–3.00	–3.32
Mn$_2$/g-CN	–3.30	–3.59
Fe$_2$/g-CN	–3.26	–3.73
Co$_2$/g-CN	–2.61	–3.10
W$_2$/g-CN	–5.28	–5.68
Re$_2$/g-CN	–4.30	–4.75

Table S5 Free energy change of six protonation steps in the urea synthesis process by distal/alternative pathway on TM_2/g-CN. The unit is eV.

TM_2/g-CN	ΔG_1	ΔG_2	ΔG_3	ΔG_4	ΔG_5	ΔG_6
Ti_2/g-CN	−1.94	0.41	−0.91	0.14/0.38	−0.18/−0.41	−0.20
Cr_2/g-CN	−0.54	−1.61	−1.03	−0.70/−1.23	−0.74–0.21	0.19
Mn_2/g-CN	−0.36	−1.86	−0.95	−0.28–0.97	−1.35/−0.66	0.28
Fe_2/g-CN	−1.92	−0.19	−1.71	−0.84/−0.64	−0.45/−0.65	−0.20
Co_2/g-CN	0.15	−2.40	−1.11	−0.05/−0.73	−1.44/−0.77	−0.40
W_2/g-CN	−0.15	−1.54	−0.72	−0.33–0.80	−0.28/0.19	0.87
Re_2/g-CN	−0.13	−1.23	−0.88	0.01/−0.63	−0.58/0.05	0.48

Table S6 Free energy change of adsorbed NCON (ΔG_{*NCON}) and the limiting potential (U_L) of urea synthesis on TM$_2$/g-CN.

TM$_2$/g-CN	ΔG_{*NCON} (eV)	U_L (V)
Ti$_2$/g-CN	−4.04	−0.41
Cr$_2$/g-CN	−2.29	−0.19
Mn$_2$/g-CN	−2.64	−0.28
Fe$_2$/g-CN	−2.02	/
Co$_2$/g-CN	−1.99	−0.15
W$_2$/g-CN	−4.96	−0.87
Re$_2$/g-CN	−3.87	−0.48
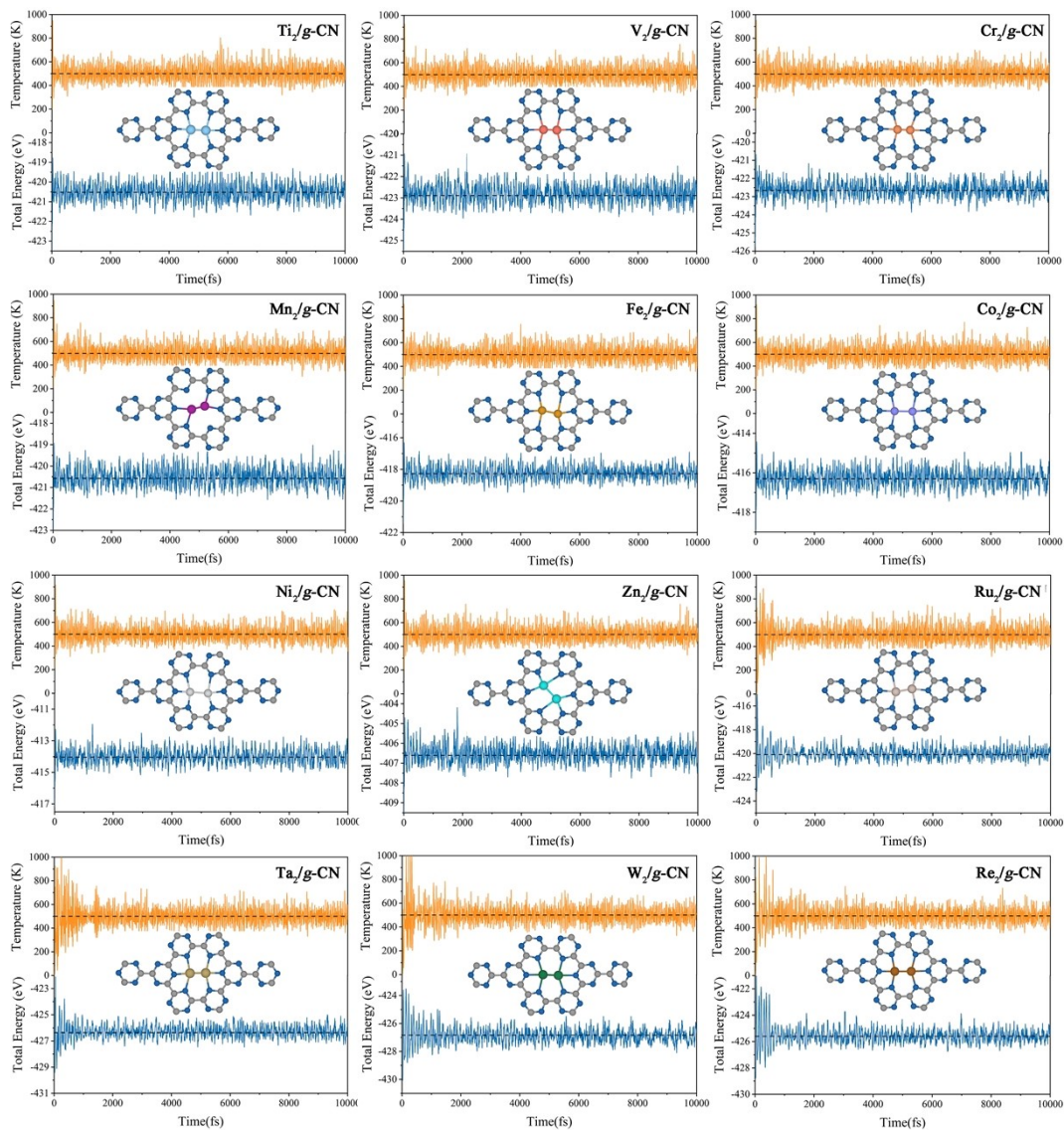
Fig. S1 Variations of temperature and energy against time from AIMD simulations for TM$_2$/g-CN. Insets are structure snapshots of TM$_2$/g-CN at 500 K after 10 ps AIMD simulations.
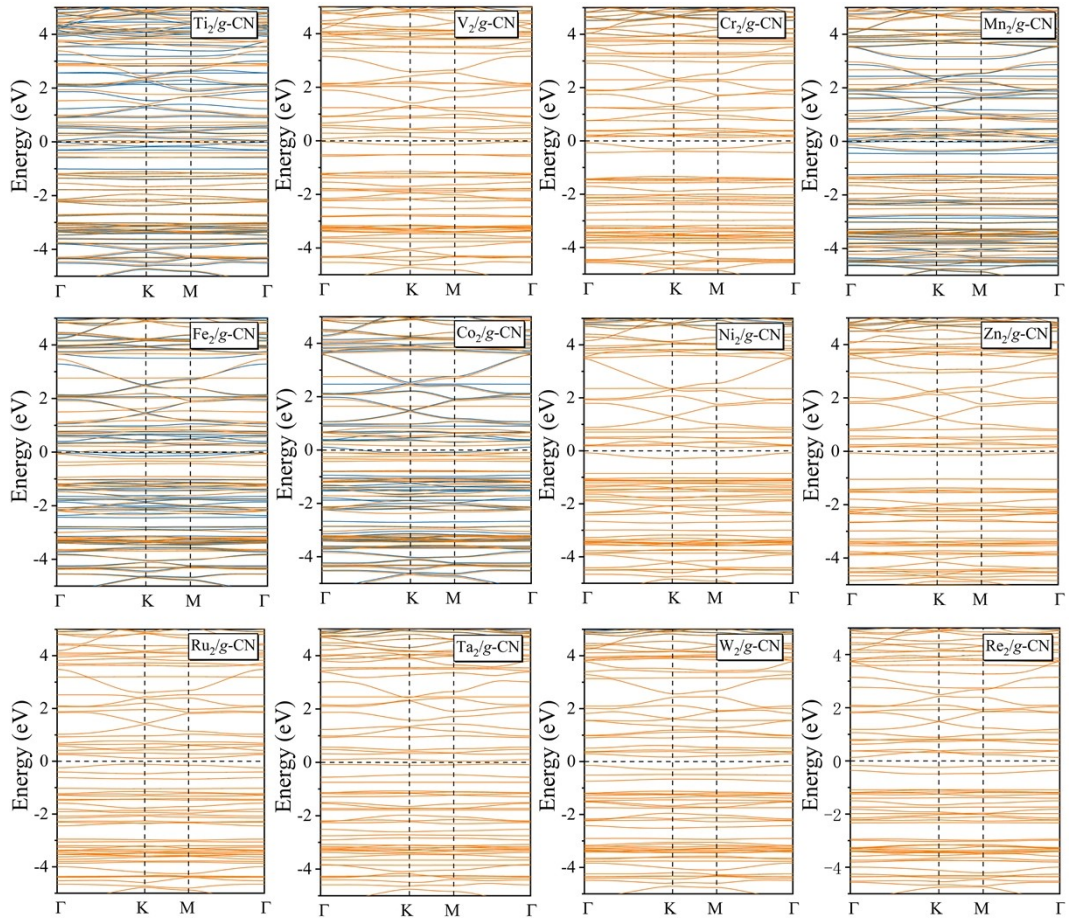
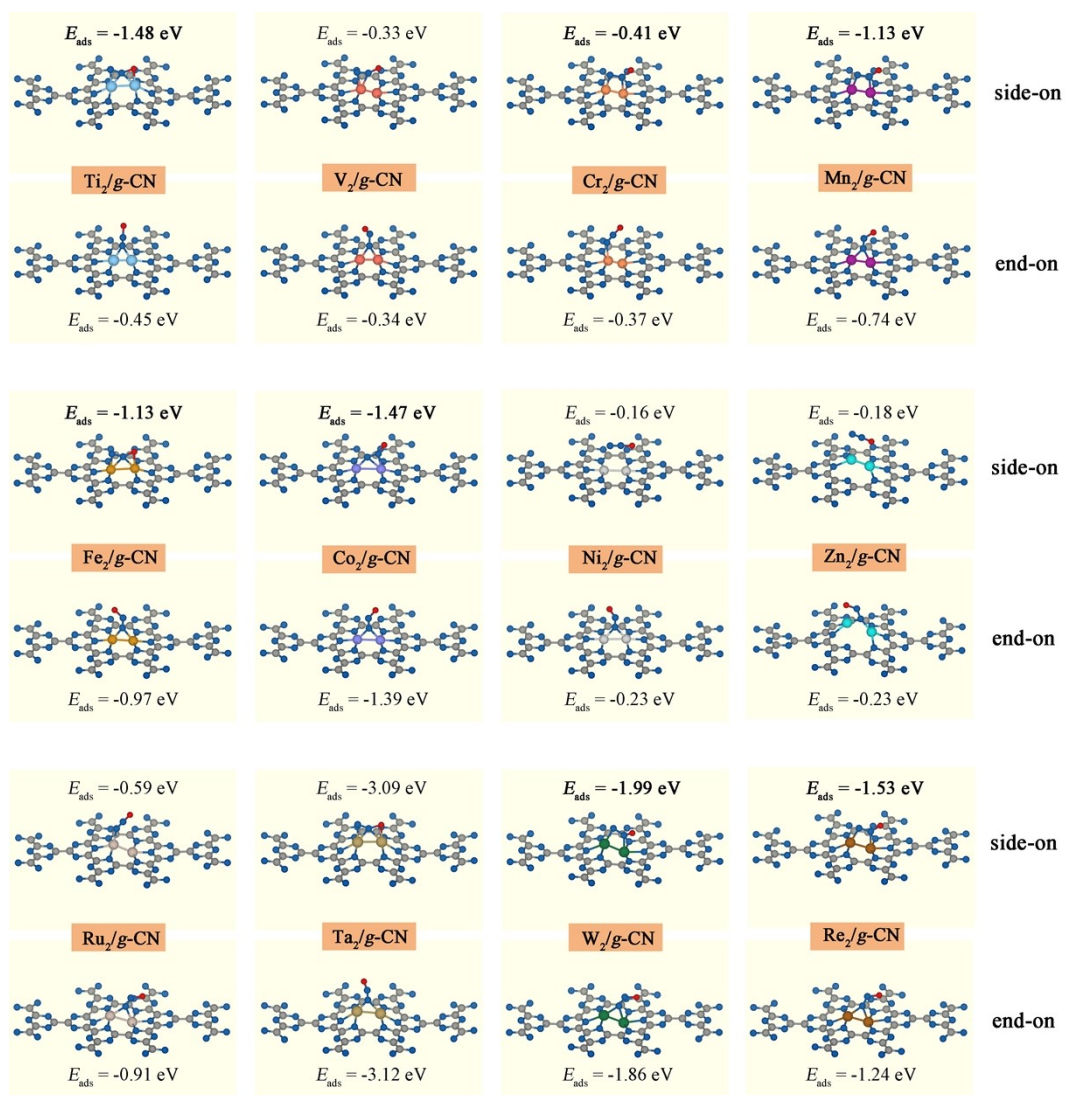**Fig. S2** Band structures of TM$_2$/g-CN. The Fermi level is set to zero.

Fig. S3 Adsorption configuration of N$_2$O on dual-TM atom active centers. N$_2$O adsorption energy (E_{ads}) is marked.
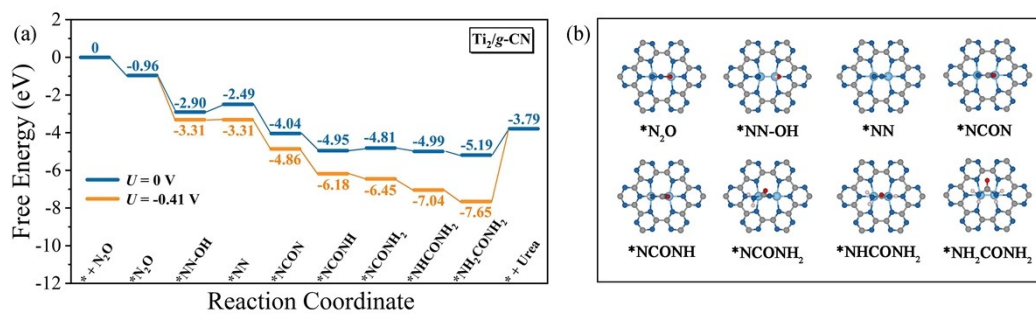
Fig. S4 (a) Gibbs free energy diagram for the urea synthesis on Ti_2/g-CN at zero (blue line) and applied potential (orange line) through distal mechanism. (b) Corresponding adsorption configurations of reaction intermediates.
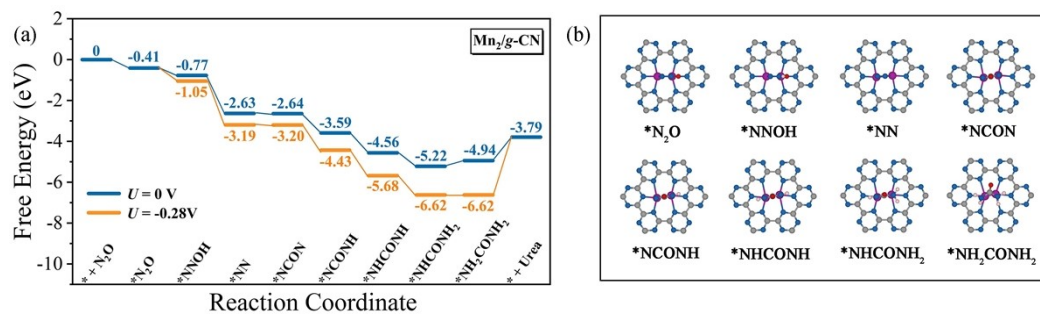
Fig. S5 (a) Gibbs free energy diagram for the urea synthesis on Mn_2/g-CN at zero (blue line) and applied potential (orange line) through alternative mechanism. (b) Corresponding adsorption configurations of reaction intermediates.
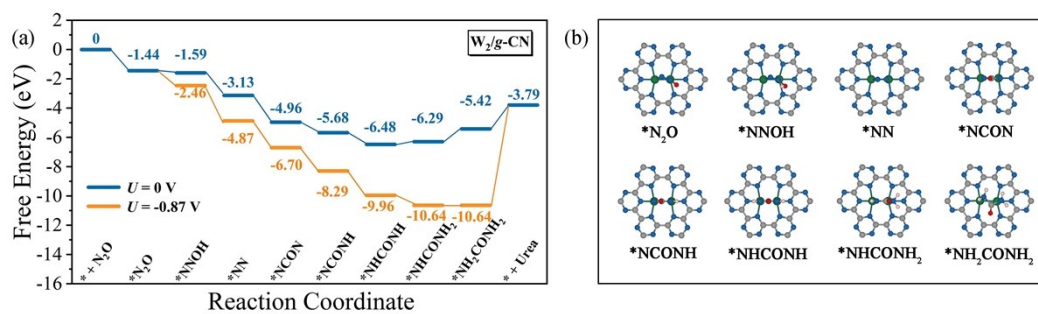
Fig. S6 (a) Gibbs free energy diagram for the urea synthesis on W_2/g-CN at zero (blue line) and applied potential (orange line) through alternative mechanism. (b) Corresponding adsorption configurations of reaction intermediates.
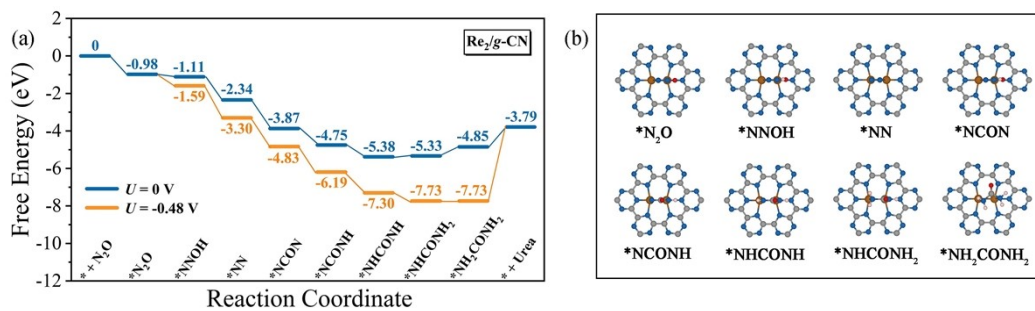
Fig. S7 (a) Gibbs free energy diagram for the urea synthesis on Re$_2$/g-CN at zero (blue line) and applied potential (orange line) through alternative mechanism. (b) Corresponding adsorption configurations of reaction intermediates.
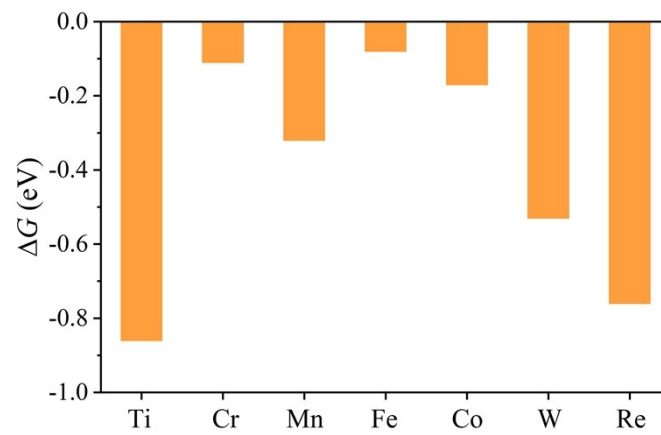
Fig. S8 Gibbs free energy difference between N_2O and H adsorption ($\Delta G = \Delta G_{*N2O} - \Delta G_{*H}$) on TM_2/g-CN.