Electronic supporting information

Mixture screening strategy of efficient transition metal heteronuclear dual-atom electrocatalysts toward nitrogen fixation

Zhouhao Zhu [a,b]†, Mengshan Chen [c]†, Mingyuzhi Sun [c], Jinhu Wang [c], Yingtang Zhou [c,]*, Xibao Li [d,]*, Hengcong Tao [b,]*

[a] *School of Port and Transportation Engineering, Zhejiang Ocean University, Zhoushan 316022, China.*
[b] *School of Petrochemical Engineering & Environment, Zhejiang Ocean University, Zhoushan 316022, China.*
[c] *National Engineering Research Center for Marine Aquaculture, Marine Science and Technology College, Zhejiang Ocean University, Zhoushan 316004, China.*
[d] *School of Materials Science and Engineering, Nanchang Hangkong University, Nanchang 330063, Chinas*

*Corresponding author.
†Show that the authors contributed equally.
E-mail: zhouyingtang@zjou.edu.cn (Y. Zhou), lixibao@nchu.edu.cn (X. Li) hengcongtao@zjou.edu.cn (H. Tao).

Table S1

Partial bond lengths of M_1M_2-NC.

Catalysts	bond length (Å)						
	M-M	M_1-N_1	M_1-N_2	M_1-N_3	M_2-N_4	M_2-N_5	M_2-N_6
AuAu-NC	2.445	1.964	2.009	1.983	1.968	2.011	1.985
AuCo-NC	2.386	1.933	2.118	1.989	1.898	1.857	1.878
AuFe-NC	2.397	1.942	2.111	1.995	1.934	1.885	1.898
AuMo-NC	2.539	1.974	2.116	1.997	2.095	2.032	2.073
CoCo-NC	2.265	1.894	1.992	1.865	1.892	1.994	1.864
FeCo-NC	2.190	1.886	2.067	1.914	1.878	2.002	1.883
FeFe-NC	2.213	1.891	2.032	1.910	1.893	2.032	1.910
FeMo-NC	2.139	1.936	2.014	1.885	2.033	2.205	2.027
MoCo-NC	2.174	2.045	2.188	1.992	1.949	1.964	1.843
MoMo-NC	2.021	1.997	2.128	2.108	1.998	2.136	2.110
RuAu-NC	2.494	2.036	1.964	1.981	1.964	2.118	1.996
RuCo-NC	2.249	1.990	2.059	1.944	1.917	1.999	1.889
RuFe-NC	2.193	2.018	2.096	1.923	1.984	1.975	1.850
RuMo-NC	2.163	1.990	2.113	1.970	2.055	2.155	2.032
RuRu-NC	2.231	2.063	2.034	1.913	2.067	2.034	1.912
TiAu-NC	2.552	1.994	1.962	2.140	1.950	2.141	2.012
TiCo-NC	2.060	2.000	2.272	2.043	1.890	2.034	1.888
TiFe-NC	2.211	2.051	2.235	2.024	1.931	2.039	1.894
TiMo-NC	2.012	1.994	2.163	2.151	1.987	2.127	2.113
TiRu-NC	2.216	2.088	2.233	2.021	2.042	2.072	1.922
TiTi-NC	2.531	2.095	1.991	2.073	2.065	2.072	2.001
TiV-NC	2.565	2.106	1.966	2.056	2.015	2.033	1.928
VAu-NC	2.484	2.051	1.965	2.009	1.959	2.141	2.003
VCo-NC	2.117	1.986	2.158	1.954	1.913	2.015	1.871
VFe-NC	2.303	2.054	2.102	1.917	1.917	1.938	1.826
VMo-NC	2.412	2.116	1.999	1.953	2.116	2.085	1.996
VRu-NC	2.224	2.052	2.077	1.937	2.041	2.051	1.912
VV-NC	2.448	2.084	1.986	1.919	2.100	1.983	1.925

Table S2

Formation energy (E_f) and adsorption energy (E_{ads}) of M_1M_2-NC and N_2 adsorbed M_1M_2-NC with side-on and end-on configurations.

Catalysts	Energy (eV)	N_2 adsorption (eV)		E_f (eV)	E_{ads} (eV)	
		side-on	end-on		side-on	end-on
AuAu-NC	-511.41	-528.08	-528.10	0.70	-0.04	-0.06
AuCo-NC	-516.81	-533.86	-533.87	-0.86	-0.42	-0.43
AuFe-NC	-517.75	-534.89	-534.88	-0.60	-0.51	-0.50
AuMo-NC	-518.50	-536.26	-536.25	1.35	-1.13	-1.13
CoCo-NC	-521.56	-538.34	-538.60	-1.77	-0.16	-0.41
FeCo-NC	-522.89	-539.52	-539.82	-1.90	0.00	-0.30
FeFe-NC	-523.75	-540.96	-540.96	-1.57	-0.58	-0.57
FeMo-NC	-525.18	-542.57	-542.15	-0.30	-0.76	-0.34
MoCo-NC	-524.11	-541.14	-541.24	-0.42	-0.40	-0.50
MoMo-NC	-526.44	-544.72	-543.94	1.14	-1.65	-0.86
RuAu-NC	-517.00	-533.89	-534.82	1.16	-0.26	-1.20
RuCo-NC	-522.29	-539.17	-539.90	-0.30	-0.25	-0.98
RuFe-NC	-523.60	-540.38	-541.03	-0.41	-0.15	-0.80
RuMo-NC	-525.27	-542.12	-542.06	0.62	-0.22	-0.16
RuRu-NC	-523.48	-540.04	-540.50	0.71	0.07	-0.39
TiAu-NC	-518.31	-535.82	-535.92	-1.56	-0.88	-0.99
TiCo-NC	-523.69	-541.21	-540.92	-3.10	-0.89	-0.59
TiFe-NC	-524.41	-541.94	-541.83	-2.62	-0.90	-0.79
TiMo-NC	-525.34	-544.34	-543.33	-0.86	-2.36	-1.36
TiRu-NC	-524.57	-541.55	-542.00	-1.78	-0.35	-0.80
TiTi-NC	-524.27	-543.47	-543.49	-2.88	-2.57	-2.59
TiV-NC	-524.90	-543.79	-542.59	-2.36	-2.26	-1.06
VAu-NC	-518.74	-535.83	-536.35	-0.83	-0.46	-0.99
VCo-NC	-523.94	-541.20	-541.33	-2.20	-0.63	-0.76
VFe-NC	-524.39	-542.39	-542.35	-1.45	-1.37	-1.33
VMo-NC	-525.15	-544.51	-544.58	0.49	-2.73	-2.80
VRu-NC	-524.78	-542.23	-542.23	-0.83	-0.82	-0.82
VV-NC	-525.40	-544.12	-542.95	-1.71	-2.09	-0.92

Table S3.

Total energy (E_{bulk}) and average energy (E_M) of metal atoms in their bulk phase and structural parameters (lattice length a and b and angle γ)

Metal	E_{bulk} (eV)	a (Å)	b (Å)	γ (degree)	E_M (eV)
Au	-12.77	4.08	4.078	90	-3.19
Co	-14.07	2.51	2.171	90	-7.03
Fe	-16.46	2.87	2.866	90	-8.23
Mo	-21.86	3.15	3.147	90	-10.93
Ru	-18.47	2.71	2.706	120	-9.23
Ti	-15.66	2.95	2.951	120	-7.83
V	-17.97	3.03	3.028	90	-8.99

Table S4.

Comparison of calculated limiting potential (U_L) of NRR on different catalysts.

Catalysts	U_L vs. CHE	References
VRu-NC	-0.21	This work
TiCo-NC	-0.23	
Ru (0001)	-0.98	[1]
Ti@N_4	-0.69	[2]
V@N_4	-0.87	
Mo_2@$V_3C_2O_2$	−0.31	[3]
Mo_3@$V_3C_2O_2$	−0.33	
W_2@$V_3C_2O_2$	−0.34	
W_3@$V_3C_2O_2$	−0.31	
Ti2-Pc	-0.75	[4]
V2-Pc	-0.39	
TiV-Pc	-0.74	
VCr-Pc	-0.85	
VTa-Pc	-0.47	
VFe-N-C	-0.36	[5]
Ru_2@GY	-0.43	[6]
Mo_3@GDY	-0.32	[7]
FeCo@GDY	-0.44	[8]
NiCo@GDY	-0.36	

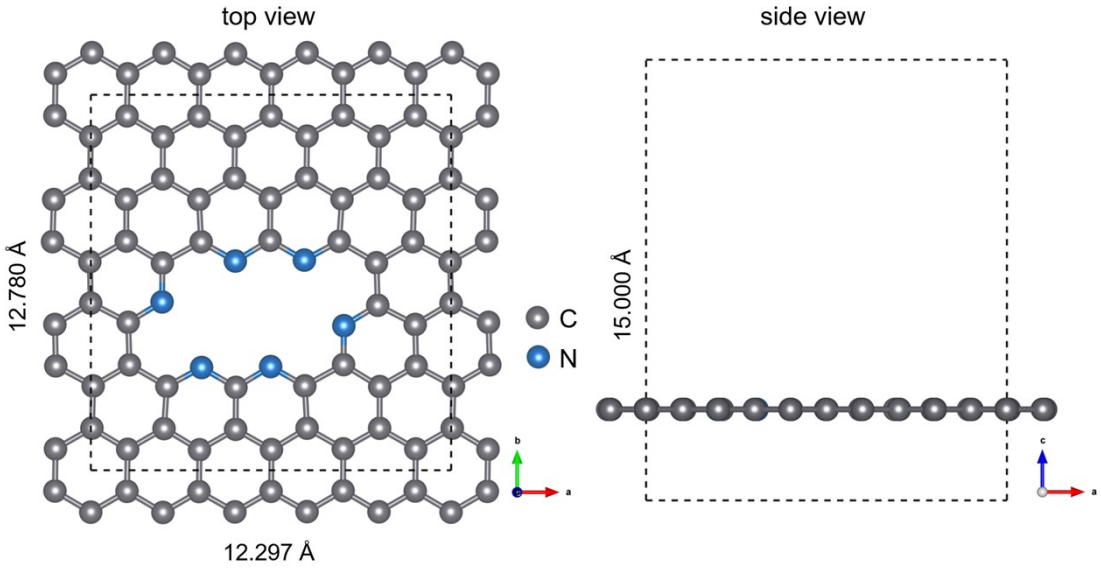

Fig. S1. Optimized structure of substrate nitrogen-doped graphene.

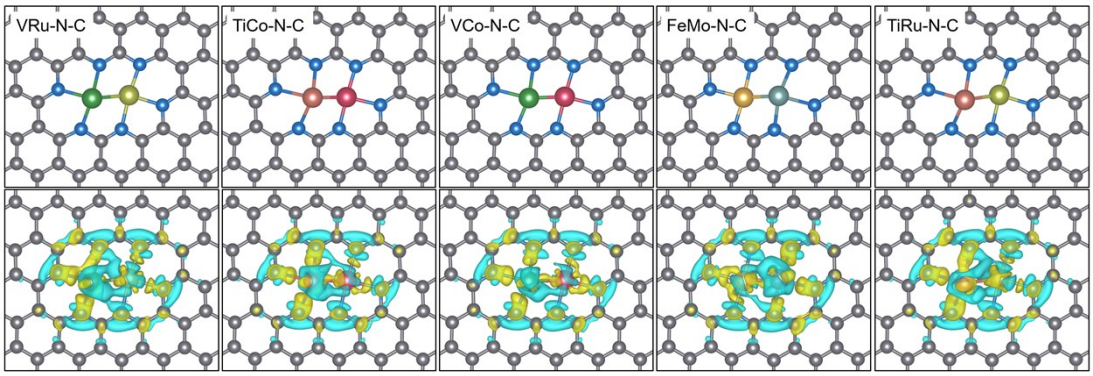

Fig. S2. Charge density differences of VRu-NC, TiCo-NC, FeMo-NC, VCo-NC and TiRu-NC. the yellow and cyan areas denote as the charge accumulation and loss, respectively. The isosurface value is set as 0.003 e/Å^3

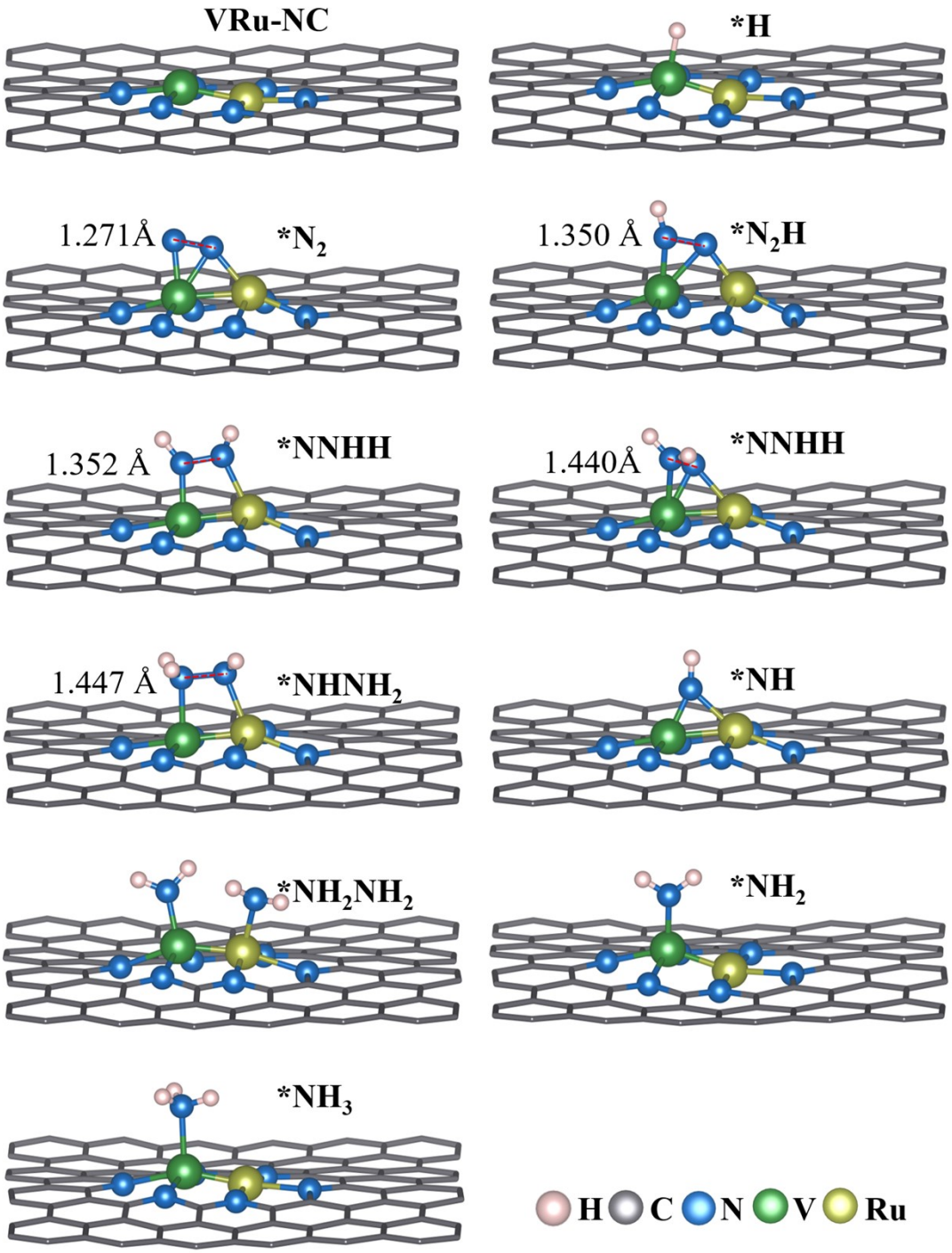

Fig. S3. Optimized structures and bond lengths of reaction intermediates on VRu-NC surface.

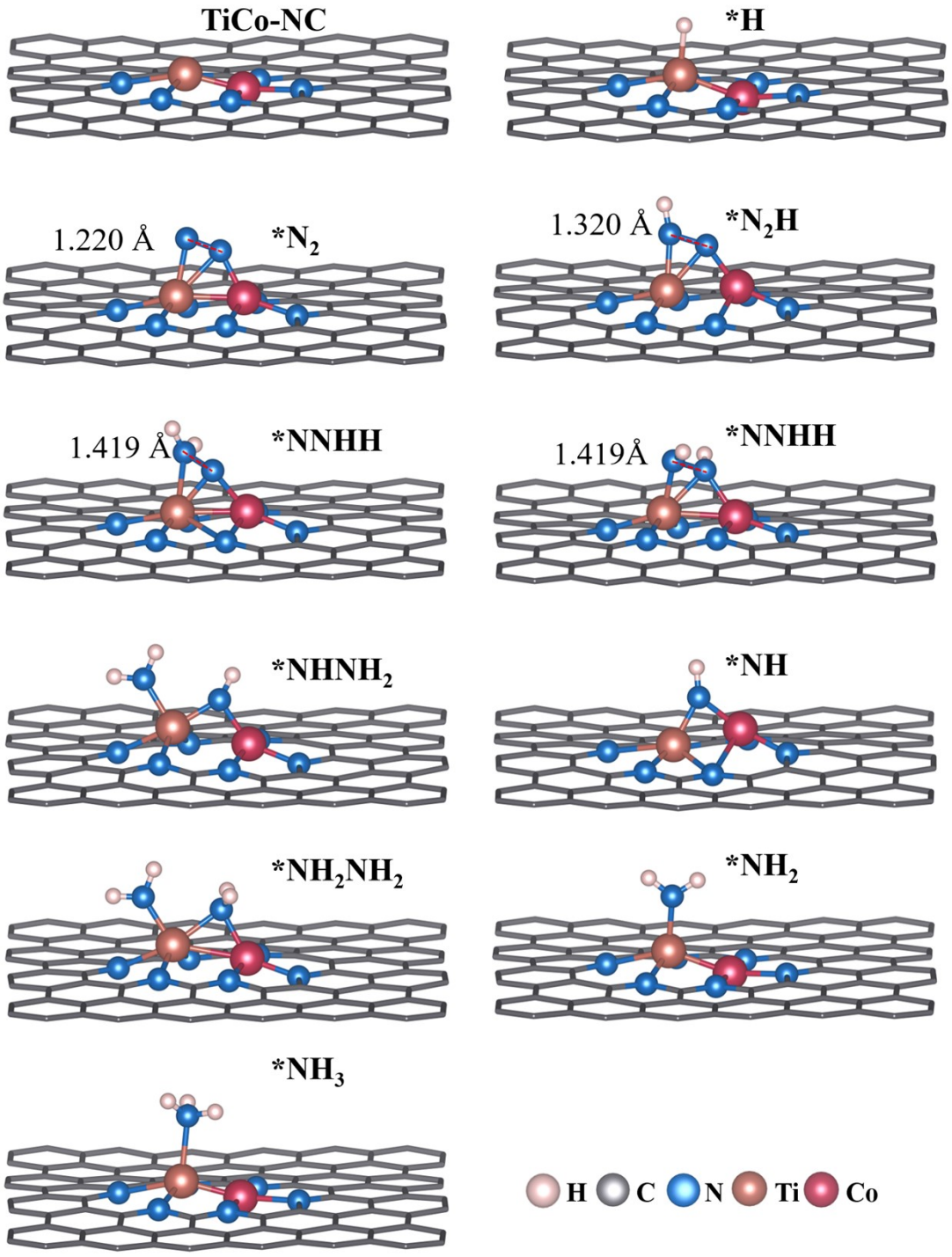

Fig. S4. Optimized structures and bond lengths of reaction intermediates on TiCo-NC surface.

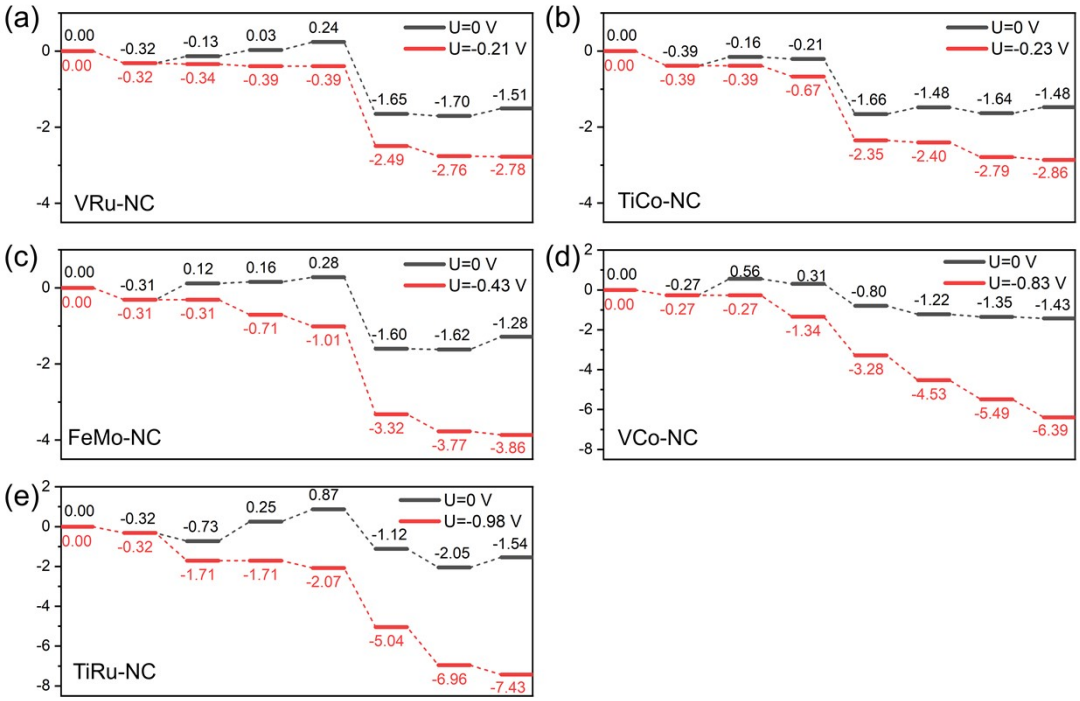

Fig. S5. The free energy diagrams for the NRR towards NH_3 and the corresponding free energy changes with the introduction of electrode potential of a) VRu-NC, b) TiCo-NC, c) FeMo-NC, d) VCo-NC and e) TiRu-NC.

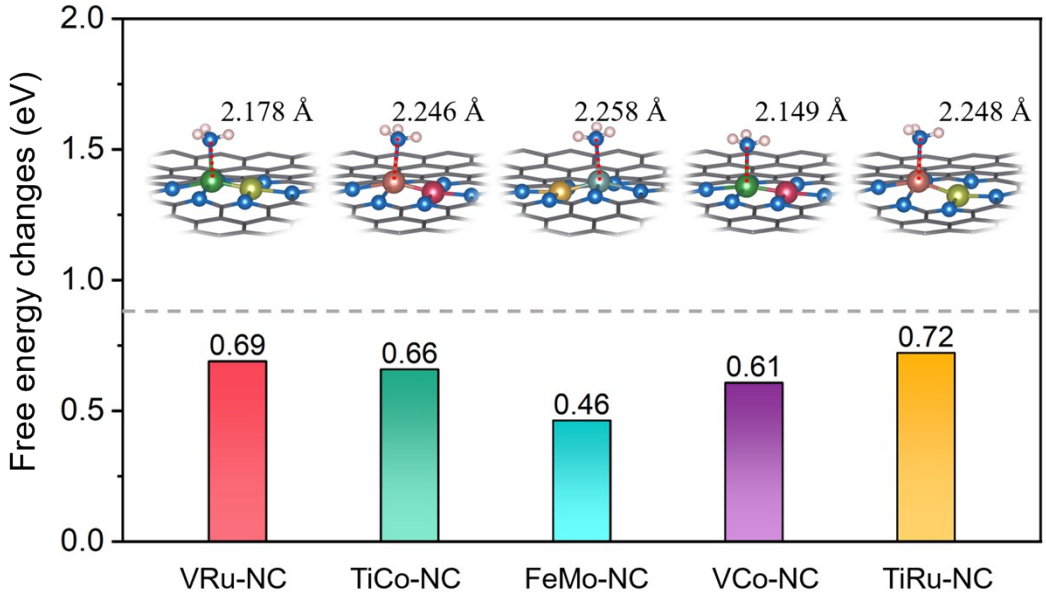

Fig. S6. Optimized structures and bond lengths of NH_3 adsorbed on surface VRu-NC, TiCo-NC, FeMo-NC, VCo-NC and TiRu-NC.

S1. The crystallographic information file of substrate nitrogen-doped graphene.

```
#======================================================================
# CRYSTAL DATA
#----------------------------------------------------------------------
data_VESTA_phase_1

_chemical_name_common                  'Graphene                                '
_cell_length_a                         12.297500
_cell_length_b                         12.780000
_cell_length_c                         15.000000
_cell_angle_alpha                      90.000000
_cell_angle_beta                       90.000000
_cell_angle_gamma                      90.000000
_cell_volume                           2357.430635
_space_group_name_H-M_alt              'P 1'
_space_group_IT_number                 1

loop_
_space_group_symop_operation_xyz
   'x, y, z'

loop_
   _atom_site_label
   _atom_site_occupancy
   _atom_site_fract_x
   _atom_site_fract_y
   _atom_site_fract_z
   _atom_site_adp_type
   _atom_site_B_iso_or_equiv
   _atom_site_type_symbol
   C1     1.0     0.003015     0.112312     0.206550     Biso    1.000000 C
   C2     1.0     0.107307     0.280879     0.206550     Biso    1.000000 C
   C3     1.0     0.006376     0.224476     0.206550     Biso    1.000000 C
   C4     1.0     0.102233     0.055782     0.206550     Biso    1.000000 C
   C5     1.0     0.203029     0.110999     0.206550     Biso    1.000000 C
   C6     1.0     0.210920     0.223531     0.206550     Biso    1.000000 C
   C7     1.0     0.301481     0.054598     0.206550     Biso    1.000000 C
   C8     1.0     0.401788     0.109127     0.206550     Biso    1.000000 C
   C9     1.0     0.402673     0.220717     0.206550     Biso    1.000000 C
   C10    1.0     0.501327     0.055074     0.206550     Biso    1.000000 C
   C11    1.0     0.600112     0.112139     0.206550     Biso    1.000000 C
   C12    1.0     0.701376     0.281491     0.206550     Biso    1.000000 C
   C13    1.0     0.593843     0.224821     0.206550     Biso    1.000000 C
   C14    1.0     0.700591     0.057075     0.206550     Biso    1.000000 C
```

C15	1.0	0.801457	0.111865	0.206550	Biso	1.000000 C
C16	1.0	0.902786	0.277976	0.206550	Biso	1.000000 C
C17	1.0	0.801721	0.222830	0.206550	Biso	1.000000 C
C18	1.0	0.901871	0.056775	0.206550	Biso	1.000000 C
C19	1.0	-0.000354	0.445101	0.206550	Biso	1.000000 C
C20	1.0	0.098306	0.610525	0.206550	Biso	1.000000 C
C21	1.0	-0.002795	0.555385	0.206550	Biso	1.000000 C
C22	1.0	0.103598	0.393950	0.206550	Biso	1.000000 C
C23	1.0	0.306139	0.608490	0.206550	Biso	1.000000 C
C24	1.0	0.198602	0.551840	0.206550	Biso	1.000000 C
C25	1.0	0.497308	0.612630	0.206550	Biso	1.000000 C
C26	1.0	0.689067	0.609875	0.206550	Biso	1.000000 C
C27	1.0	0.796294	0.439436	0.206550	Biso	1.000000 C
C28	1.0	0.893639	0.608894	0.206550	Biso	1.000000 C
C29	1.0	0.792655	0.552530	0.206550	Biso	1.000000 C
C30	1.0	0.900257	0.388272	0.206550	Biso	1.000000 C
C31	1.0	-0.001826	0.776525	0.206550	Biso	1.000000 C
C32	1.0	0.100388	0.943955	0.206550	Biso	1.000000 C
C33	1.0	-0.000308	0.888470	0.206550	Biso	1.000000 C
C34	1.0	0.098588	0.721456	0.206550	Biso	1.000000 C
C35	1.0	0.199436	0.776200	0.206550	Biso	1.000000 C
C36	1.0	0.300016	0.943423	0.206550	Biso	1.000000 C
C37	1.0	0.199984	0.887695	0.206550	Biso	1.000000 C
C38	1.0	0.299920	0.721148	0.206550	Biso	1.000000 C
C39	1.0	0.398680	0.778242	0.206550	Biso	1.000000 C
C40	1.0	0.500242	0.944087	0.206550	Biso	1.000000 C
C41	1.0	0.399758	0.889211	0.206550	Biso	1.000000 C
C42	1.0	0.498207	0.724235	0.206550	Biso	1.000000 C
C43	1.0	0.598530	0.778742	0.206550	Biso	1.000000 C
C44	1.0	0.700056	0.945577	0.206550	Biso	1.000000 C
C45	1.0	0.600000	0.889890	0.206550	Biso	1.000000 C
C46	1.0	0.696963	0.722377	0.206550	Biso	1.000000 C
C47	1.0	0.797807	0.777531	0.206550	Biso	1.000000 C
C48	1.0	0.900353	0.944819	0.206550	Biso	1.000000 C
C49	1.0	0.799647	0.889334	0.206550	Biso	1.000000 C
C50	1.0	0.897037	0.721023	0.206550	Biso	1.000000 C
N1	1.0	0.307368	0.273597	0.206550	Biso	1.000000 N
N2	1.0	0.499015	0.276122	0.206550	Biso	1.000000 N
N3	1.0	0.197650	0.448327	0.206550	Biso	1.000000 N
N4	1.0	0.400986	0.557193	0.206550	Biso	1.000000 N
N5	1.0	0.592614	0.559775	0.206550	Biso	1.000000 N
N6	1.0	0.702261	0.384988	0.206550	Biso	1.000000 N

References

1. E. Skulason, T. Bligaard, S. Gudmundsdottir, F. Studt, J. Rossmeisl, F. Abild-Pedersen, T. Vegge, H. Jonsson and J. K. Norskov, *Phys Chem Chem Phys*, 2012, **14**, 1235-1245.
2. C. Choi, S. Back, N. Kim, J. Lim, Y. Kim and Y. Jung, *ACS Catal.*, 2018, **8**, 7517-7525.
3. J. Wan, Y. Wang, W. Tian, H. Zhang and Y. Wang, *Appl. Surf. Sci.*, 2021, **569**, 151020.
4. X. Guo, J. Gu, S. Lin, S. Zhang, Z. Chen and S. Huang, *J. Am. Chem. Soc.*, 2020, **142**, 5709-5721.
5. C. N. Sun, Z. L. Wang, X. Y. Lang, Z. Wen and Q. Jiang, *ChemSusChem*, 2021, **14**, 4593-4600.
6. L. Jasin Arachchige, Y. Xu, Z. Dai, X. Zhang, F. Wang and C. Sun, *J. Phys. Chem. C*, 2020, **124**, 15295-15301.
7. M. Li, Y. Cui, X. Zhang, Y. Luo, Y. Dai and Y. Huang, *J. Phys. Chem. Lett.*, 2020, **11**, 8128-8137.
8. D. Ma, Z. Zeng, L. Liu and Y. Jia, *J. Energy Chem.*, 2021, **54**, 501-509.