Supporting Information for

Ruthenium Single-Atom Catalysis for Electrocatalytic Nitrogen

Reduction Unveiled by Grand Canonical Density Functional Theory

Yujin Ji[1]*, Yifan Li[2], Huilong Dong[3], Lifeng Ding[4] and Youyong Li[1]*

[1] *Institute of Functional Nano & Soft Materials (FUNSOM), Jiangsu Key Laboratory for Carbon-Based Functional Materials & Devices, Soochow University, Suzhou, Jiangsu 215123, China*

[2] *Key Laboratory for Liquid-Solid Structural Evolution and Processing of Materials, Ministry of Education, Shandong University, Jinan, Shandong 250061, China*

[3] *School of Materials Engineering, Changshu Institute of Technology, Changshu, Jiangsu 215500, China*

[4] *Department of Chemistry, Xi'an JiaoTong-Liverpool University, 111 Ren'ai Road, Suzhou Dushu Lake, Higher Education Town, Jiangsu Province 215123, China*

*Corresponding author

Supplementary Note S1

It should be noted that the definition of the grand canonical energy Ω in this manuscript is different with that in the JDFTx manual [1] because we adopt a different energy reference. In the JDFTx manual, they view the single-electron energy as a reference so the E_{SCF} needs to subtract all-electron energy contribution while in our method, the energy in the constant charge model is set as a standard and we only need to consider the electron change. We can prove that this definition difference has no influence on the relative energy/adsorption energy, namely

$$\Delta G = \Delta \Omega$$

Detailed derivation is as follows:

Step 1: (Definition of physical parameters)

μ_e: Electronic chemical potential, namely -4.66 in U=0 V/SHE.

E_{SCF}/F: Total energy in the SCF calculation

N_0: Total valance electron number

N: Optimized valance electron number at a fixed electrode potential

$N_e = N - N_0$: Number of valance electron change

Step 2: (Deduction)

JDFTx definition of the **grand free energy** $G = F - N\mu_e = E_{SCF} - N\mu_e$

Our definition of the **grand canonical energy** $\Omega = E_{SCF} + N_e \mu_e$

For a simple reaction A+B→AB,

$$\Delta G = E_{SCF}(AB) - N(AB)\mu_e - \left[E_{SCF}(A) - N(A)\mu_e + E_{SCF}(B) - N(B)\mu_e \right]$$

$$= E_{SCF}(AB) - E(A) - E(B) + [N(A) + N(B) - N(AB)]\mu_e$$

$$= E_{SCF}(AB) - E(A) - E(B) + [N_0(A) + N_e(A) + N_0(B) + N_e(B)$$
$$\mu_e$$

$$= \Omega(AB) - \Omega(A) - \Omega(B) + \left[N_0(A) + N_0(B) - N_0(AB)\right]\mu_e$$

$$= \Delta\Omega$$

Thus,

$$\Delta G = \Delta\Omega$$

As a quantitative example, we proved that this energy definition has no influence on the adsorption free energy of $*N_2$.

Ru-N$_4$	E_{SCF}/F (eV)	N_0	N	N_e	μ_e (eV)	G (eV)	Ω (eV)
N$_2$	-398.45	10	10.00	0.00	-4.66	-589.74	-543.14
*	-12030.26	252	251.23	-0.77	-4.66	-13231.10	-12056.78
*N$_2$	-12604.90	262	261.21	-0.79	-4.66	-13822.10	-12601.18

$$\Delta G = G(*N_2) - G(N_2) - G(*) = -1.27$$

$$\Delta\Omega = \Omega(*N_2) - \Omega(N_2) - \Omega(*) = -1.27$$

References
[1] http://jdftx.org/FixedPotential.html

Supplementary Note S2

Figure S1 clearly indicates that the Ru-N$_4$ motifs with -1.0, 0.0 and 1.0 net electrons after 5 ps MD tended to be equilibrized and the final configurations of Ru-N$_4$ still retained their integrities. Therefore, the GC-DFT has no influence on the stability of the Ru-N$_4$ catalysts under realistic conditions.
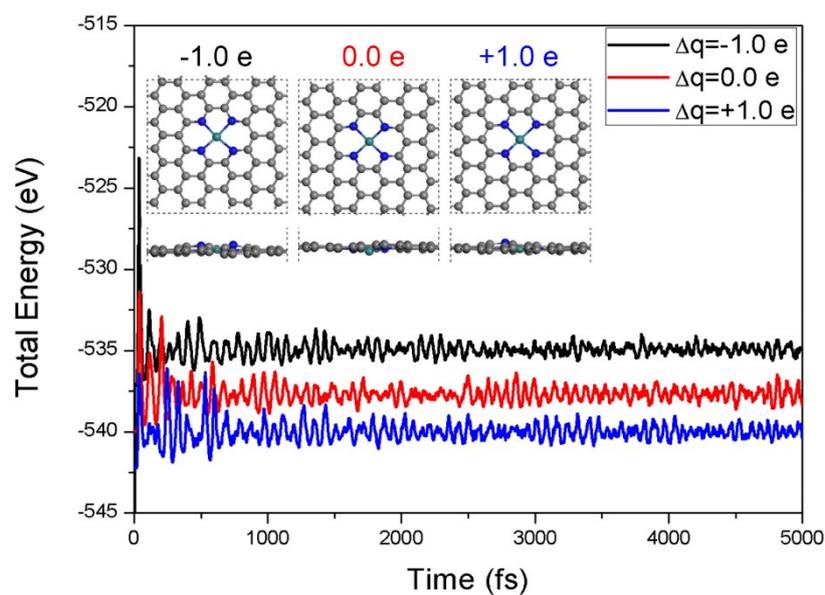
Figure S1. 5 *ps ab initio* molecular dynamic trajectories of the Ru-N$_4$ motifs with net charges of (a) -1.0, (b) 0.0 and (c) +1.0 electron. The insert is the top view and side view of the relaxed geometry configurations at the final state.
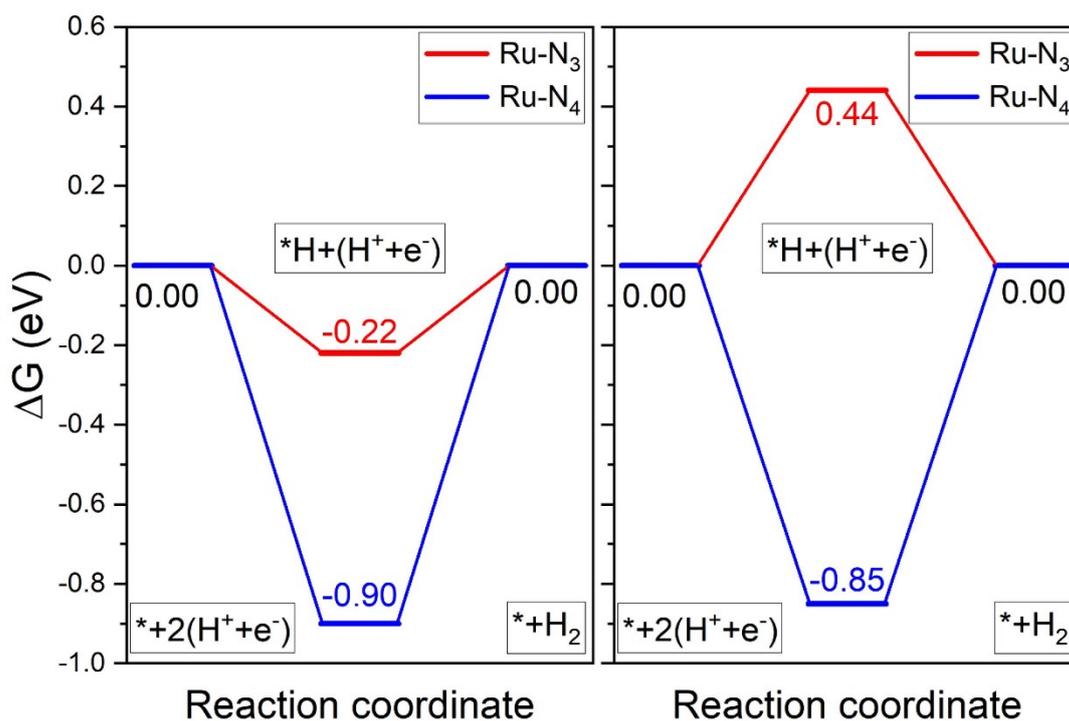
Figure S2. Free energy evolution diagrams for the hydrogen evolution reaction on Ru-N$_3$ and Ru-N$_4$ sites. The left and right are corresponding to the CCM and CPM, accordingly.

Table S1. Adsorption free energies of *N$_2$ and *H on Ru-N$_3$ and Ru-N$_4$ reaction sites based on the CCM and CPM.

ΔG (eV)	CCM		CPM	
	*N$_2$	*H	*N$_2$	*H
Ru-N$_3$	**-0.99**	-0.22	**-0.64**	0.44
Ru-N$_4$	**-1.17**	-0.90	**-1.08**	-0.85