Electronic Supplementary Material (ESI) for ChemComm.

Nitrogen-fixation catalyst based on graphene: every part counts

Yuan-Qi Le, Jia Gu, Wei Quan Tian*

State Key Laboratory of Urban Water Resource and Environment, Institute of Theoretical and Simulational Chemistry, Academy of Fundamental and Interdisciplinary Sciences, Harbin Institute of Technology, Harbin, 150080, P. R. China

**Corresponding author: tianwq@hit.edu.cn*

Supporting Information

Reference of Gaussian 03 package, B3LYP method, basis sets 6-31G(d,p) and SDD:

1. Gaussian 03

Gaussian 03, Revision E.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, Gaussian, Inc., Wallingford CT, 2004.

2. B3LYP

(a) C. Lee, W. Yang, and R. G. Parr, *Phys. Rev. B* 1988, **37**, 785-789. (b) A. D. Becke, *J. Chem. Phys.* 1993, **98**, 5648-5652.

3. 6-31G(d,p)

(a) W. J. Hehre, R. Ditchfield, and J. A. Pople, *J. Chem. Phys.* 1972, 56, 2257-2261. (b) G. A. Petersson, A. Bennett, T. G. Tensfeldt, M. A. AI-Laham, W. A. Shirley, and J. Mantzaris, *J. Chem. Phys.* 1988, **89**, 2193-2218.

4. SDD

D. Andrae, U. Haeussermann, M. Dolg, H. Stoll, and H. Preuss, *Theor. Chem. Acc.,* 1990, **77**, 123-141.

Table S1. The bond distance, bond angle of the MoN_3 part (the label of N atoms is shown in Figure S1) in $C_{33}H_{15}MoN_3$, $C_{69}H_{21}MoN_3$ and $C_{117}H_{27}MoN_3$.

bond length	Mo-N1	Mo-N2	Mo-N3	Mo-N1N2	Mo-N2N3	Mo-N1N3	NNN-Mo
$C_{33}H_{15}MoN_3$	1.96	1.96	1.96	91.3	91.3	91.3	53.8
$C_{69}H_{21}MoN_3$	1.96	1.96	1.96	91.3	91.3	91.3	53.8
$C_{117}H_{27}MoN_3$	1.95	1.95	1.95	91.8	91.8	91.8	53.4

Table S2. The bond distances of the MoN_3 part (the label of N atoms is shown in Figure S1) of $C_{33}H_{15}MoN_3/N_2$ and $C_{69}H_{21}MoN_3/N_2$ before and after the addition of the first H^+ in the enzymatic catalytic reaction path.

Bond	N_2(ad)		H1		H1R	
length	$C_{33}H_{15}MoN_3$	$C_{69}H_{21}MoN_3$	$C_{33}H_{15}MoN_3$	$C_{69}H_{21}MoN_3$	$C_{33}H_{15}MoN_3$	$C_{69}H_{21}MoN_3$
Mo-N1	2.11	2.10	2.13	2.12	2.07	2.07
Mo-N2	1.99	1.98	2.02	2.02	2.05	2.05
Mo-N3	1.99	1.98	2.02	2.00	2.05	2.05
Nα-Nβ	1.21	1.21	1.29	1.28	1.30	1.30
Mo-Nα	2.02	2.02	1.90	1.97	1.91	1.91
Mo-Nβ	2.04	2.03	2.01	1.98	2.04	2.04
Nβ-H			1.02	1.02	1.02	1.02

Table S3. Mulliken charge of the three groups (the division into three groups is illustrated in Figures S1and S2) in $C_{33}H_{15}MoN_3$, $C_{69}H_{21}MoN_3$ and $C_{117}H_{27}MoN_3$.

net charge	grp3(t)	grp3(a)	grp2(t)	grp2(a)	Mo	N1	N2	N3
$C_{33}H_{15}MoN_3$	1.24	0.082	0.00	0.000	0.86	–0.70	–0.70	–0.70
$C_{69}H_{21}MoN_3$	1.74	0.083	–0.43	–0.006	0.90	–0.73	–0.73	–0.73
$C_{117}H_{27}MoN_3$	2.27	0.084	–0.94	–0.008	0.89	–0.74	–0.74	–0.74

Table S4. Variation of Mulliken charge of different groups (grp) in Mo/N graphenes before and after loss of an electron.

charge variation	$C_{33}H_{15}MoN_3$	$C_{69}H_{21}MoN_3$	$C_{117}H_{27}MoN_3$
grp1	0.05	0.03	–0.02
grp2	0.37	0.43	0.51
grp3	0.58	0.54	0.51

Table S5. Reaction energies(kJ/mol), N-N bond length (Å) and bond order in the Schrock(Schrk) and enzymatic(Enzym) reaction as shown in Figure 3. Hn is the addition of the nth proton and HnR is the reduction after the nth protonation (as shown in Figure 6). The number (1-15) in parenthesis of reaction step is the order of reaction process in Figure 2. S in parenthesis stands for Schrock and E in parenthesis stands for enzymatic.

Reaction step	Reaction energy		bond length/N-N		bond order/N-N		total bond order/Mo	
	Schrk	Enzym	Schrk	Enzym	Schrk	Enzym	Schrk	Enzym
N_2+Mo(1)	0	0					4.17	4.17
N_2(ad)(2)	–104.1	–143.9	1.13	1.21	2.58	2.03	4.53	4.94
H1(3)	–131.1	–156.0	1.23	1.29	1.75	1.53	4.81	5.28
H1R(4)	–181.4	–211.3	1.24	1.30	1.74	1.47	4.48	4.65
H2(5)	–323.1	–294.7	1.32	1.38	1.25	1.21	4.59	4.51
H2R(6)	–331.6	–326.4	1.33	1.39	1.20	1.18	4.79	4.93
H3(7)	–228.2	–420.4	1.44	1.42	0.97	1.05	4.73	4.59
H3R(8)	–318.6	–484.9	1.43	1.43	0.99	1.02	4.43	4.15
H4(9)	–678.3	–516.8	2.91	1.46	0.03	1.01	4.54	3.89
H4R(10)	–682.2	–497.0	3.01	1.46	0.02	1.00	4.73	4.33
NH(S)/H5(E)(11)	–661.3	–789.8		3.02				
H5(S)/H5R(E)(12)	–758.5	–858.7		3.09				
H5R(S)/NH_2(E)(13)	–839.0	–839.0						
H6(14)	–898.8	–898.8						
H6R(15)	–890.3	–890.3						

Table S6. Variation of Mulliken charge of the three groups (as shown in Figure 5) in the catalyst during the enzymatic protonation of N_2 (the charge difference of the present step from that of the previous step). The number in parenthesis is the average charge variation per atom. More effective numbers of digit is kept for some values for comparison.

charge variation	1st	2nd	3rd	4th	5th	6th	average
grp1 (active center)	0.12 (0.03)	0.09 (0.02)	0.07 (0.02)	–0.12 (–0.03)	0.14 (0.03)	–0.16 (–0.04)	0.022 (0.006)
grp2 (transmitter)	0.05 (0.002)	0.02 (0.001)	–0.048 (–0.002)	–0.06 (–0.002)	0.23 (0.01)	–0.04 (–0.002)	0.025 (0.001)
grp3 (reservoir)	0.75 (0.031)	0.79 (0.03)	0.65 (0.027)	0.66 (0.03)	1.00 (0.04)	0.66 (0.03)	0.75 (0.031)
total	0.92	0.90	0.67	0.48	1.37	0.46	0.80

Table S7. Variation of Mulliken charge (the charge difference of the present step from that of the previous step) of the three groups (shown in Figure 5) in the catalyst during the enzymatic reduction.

charge variation	1st	2nd	3rd	4th	5th	6th	average
grp1 (active center)	–0.04 (–0.01)	–0.07 (–0.02)	–0.09 (–0.02)	–0.05 (–0.01)	–0.04 (–0.01)	–0.06 (–0.02)	–0.06 (–0.02)
grp2 (transmitter)	–0.02 (–0.001)	–0.08 (–0.003)	0.03 (0.001)	–0.08 (–0.003)	–0.07 (–0.003)	–0.09 (–0.004)	–0.05 (–0.002)
grp3 (reservoir)	–0.82 (–0.03)	–0.79 (–0.03)	–0.79 (–0.03)	–0.82 (–0.03)	–0.84 (–0.04)	–0.83 (–0.04)	–0.81 (–0.03)
total	–0.88	–0.94	–0.85	–0.95	–0.95	–0.98	–0.92

Table S8. Variation of natural charge of the three groups (as shown in Figure 5) in the catalyst during the enzymatic protonation of N_2 (the charge difference of the present step from that of the previous step) in $C_{33}H_{15}MoN_3$.

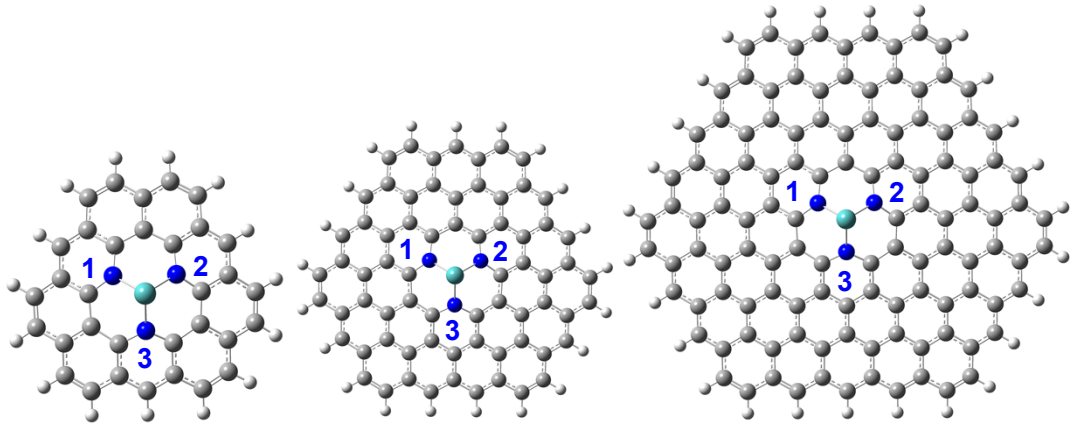
charge variation	1st	2nd	3rd	4th	5th	6th
grp1 (active center)	–0.13	0.04	0.03	–0.01	0.26	–0.12
grp2 (transmitter)	0.26	–0.03	0.00	–0.04	0.12	-0.15
grp3 (reservoir)	1.04	0.78	0.62	0.52	1.22	0.74
total	1.17	0.79	0.65	0.47	1.6	0.47

Table S9. Variation of natural charge (the charge difference of the present step from that of the previous step) of the three groups (shown in Figure 5) in the catalyst during the enzymatic reduction.

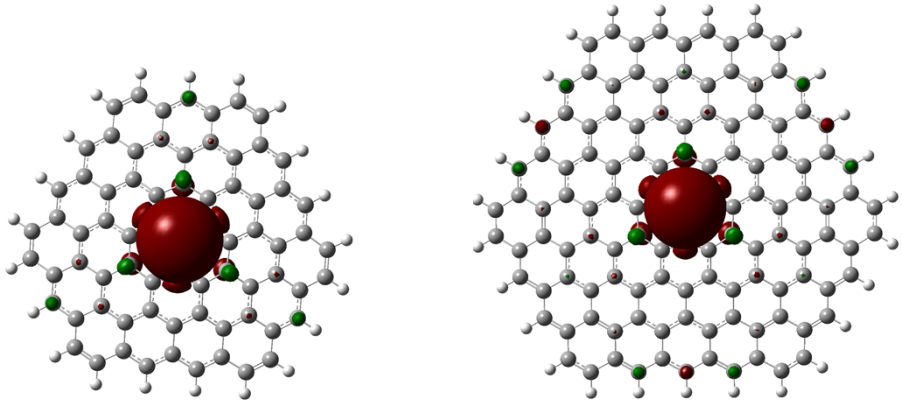
charge variation	1st	2nd	3rd	4th	5th	6th
grp1 (active center)	0.01	–0.02	–0.04	–0.17	0.04	–0.06
grp2 (transmitter)	–0.03	–0.02	-0.13	–0.12	–0.004	0.00
grp3 (reservoir)	–0.85	–0.86	–0.76	–0.69	–1.00	–0.92
total	–0.87	–0.90	–0.93	–0.95	–0.95	–0.98

Table S10. Mulliken charge of the three groups (as shown in Figure 5) in the catalyst during the reaction steps.

Reaction step	grp1		grp2		grp3		N_2+H		total
	total	average	total	average	total	average	total	average	
N_2+Mo(1)	–1.24	–0.309	1.58	0.067	–0.34	–0.014			0.0
N_2(ad)(2)	–1.13	–0.284	1.62	0.067	–0.23	–0.010	–0.25	–0.125	0.0
H1(3)	–0.89	–0.223	1.75	0.073	0.54	0.023	–0.40	–0.132	1.0
H1R(4)	-0.95	–0.237	1.71	0.071	–0.29	–0.012	–0.48	–0.159	0.0
H2(5)	–0.90	–0.226	1.76	0.073	0.52	0.022	–0.38	–0.095	1.0
H2R(6)	–0.97	–0.243	1.69	0.070	–0.62	–0.011	–0.45	–0.112	0.0
H3(7)	–0.91	–0.226	1.64	0.068	0.39	0.016	–0.12	–0.023	1.0
H3R(8)	–0.99	–0.248	1.67	0.070	–0.40	–0.017	–0.28	–0.056	0.0
H4(9)	–1.11	–0.278	1.61	0.067	0.26	0.011	0.24	0.040	1.0
H4R(10)	–1.17	–0.292	1.53	0.064	–0.56	–0.023	0.20	0.032	0.0
NH(S)/H5(E)(11)	–1.03	–0.257	1.76	0.073	0.44	0.018	–0.17	–0.024	1.0
H5(S)/H5R(E)(12)	–1.07	–0.267	1.69	0.070	–0.40	–0.017	–0.22	–0.031	0.0
H5R(S)/NH_2(E)(13)	–1.04	–0.259	1.70	0.071	–0.34	–0.014	–0.33	–0.110	0.0
H6(14)	–1.18	–0.294	1.65	0.069	0.32	0.013	0.21	0.052	1.0
H6R(15)	–1.24	–0.309	1.56	0.065	–0.51	–0.021	0.19	0.047	0.0



$C_{33}H_{15}MoN_3$ **$C_{69}H_{21}MoN_3$** **$C_{117}H_{27}MoN_3$**



$C_{69}H_{21}MoN_3$ **$C_{117}H_{27}MoN_3$**

Figure S1. Three models for the Mo/N-doped graphene catalyst and the lowest unoccupied molecular orbital of Mo/N-doped graphenes ($C_{69}H_{21}MoN_3$ and $C_{117}H_{27}MoN_3$).

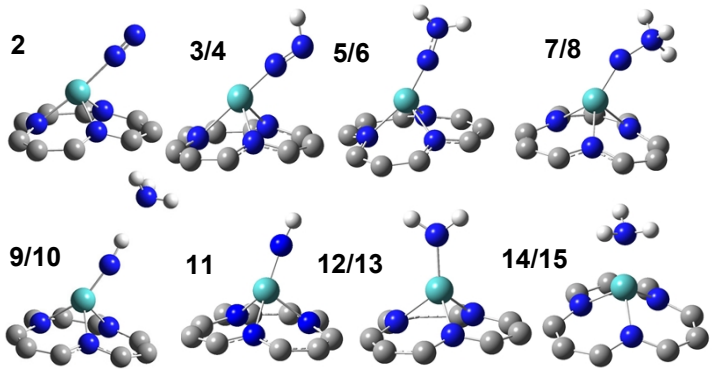


Figure S2. The structures of the intermediates in the Schrock reaction path. 2-N_2 adsorption, 3/4-1st hydrogenation (protonation and reduction), 5/6-2nd hydrogenation, 7/8-3rd hydrogenation, 9/10-4th hydrogenation, 11-ammonia desorption, 12/13-5th hydrogenation, 14/15-6th hydrogenation. The number of intermediate is the same to that in Fig. 2. (N in blue, C in gray, H in white, Mo in light blue).

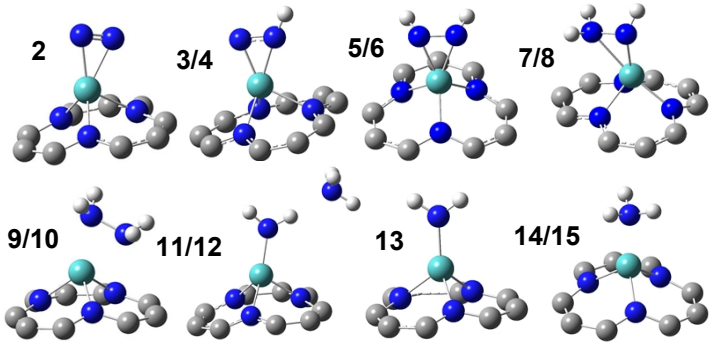


Figure S3. The structures of the intermediates in the enzymatic reaction path. 2-N_2 adsorption, 3/4-1st hydrogenation (protonation and reduction), 5/6-2nd hydrogenation, 7/8-3rd hydrogenation, 9/10-4th hydrogenation,11/12-5th hydrogenation, 13-ammonia desorption, 14/15-6th hydrogenation. The number of intermediate is the same to that in Fig. 2. (N in blue, C in gray, H in white, Mo in light blue).

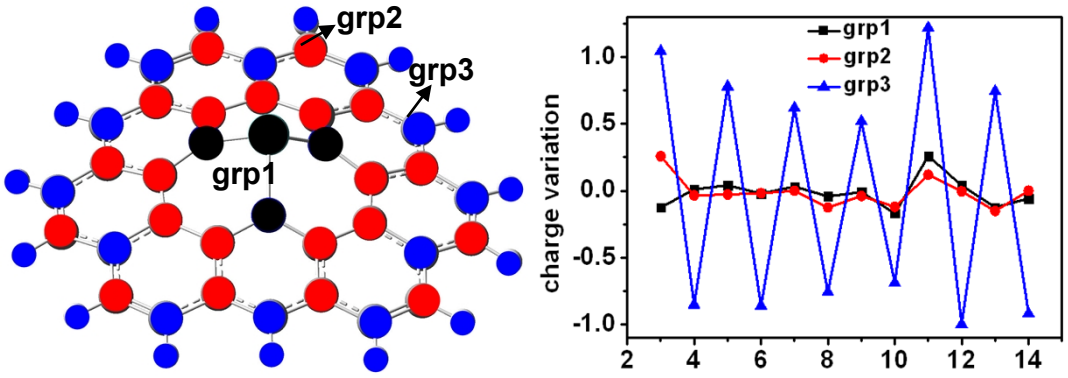


Figure S4. The variation of natural charge (the charge difference of the present step from that of the previous step) of different groups (grp) in Mo/N graphene ($C_{33}H_{15}MoN_3$) during the enzymatic catalytic N_2 fixation. The numbering of the reaction steps is shown in Figure 2.

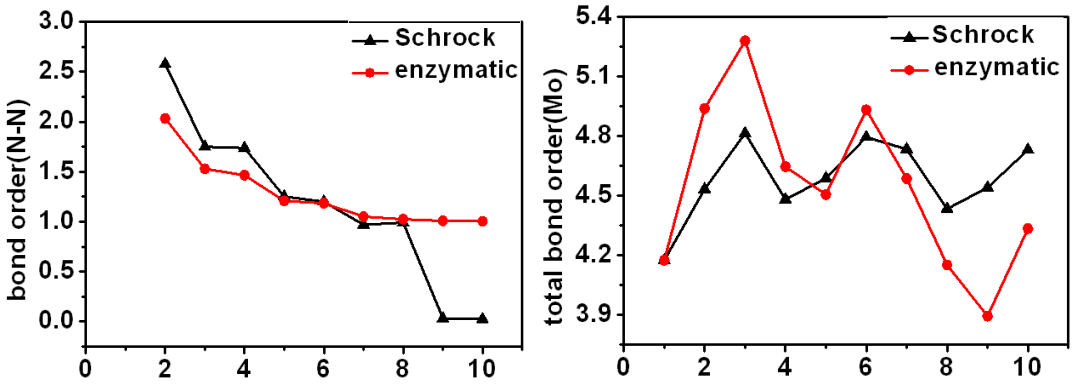


Figure S5. The N-N bond order and the total bond order of Mo during the N_2 fixation in the Schrock and enzymatic reaction paths. 1-catalyst, 2-N_2 adsorption, 3/4-1st hydrogenation (protonation and reduction), 5/6-2nd hydrogenation, 7/8-3rd hydrogenation, 9/10-4th hydrogenation.