Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supporting information

Hydrogen Peroxide Synthesis on Porous Graphitic Carbon Nitride Using Water as Hydrogen Source

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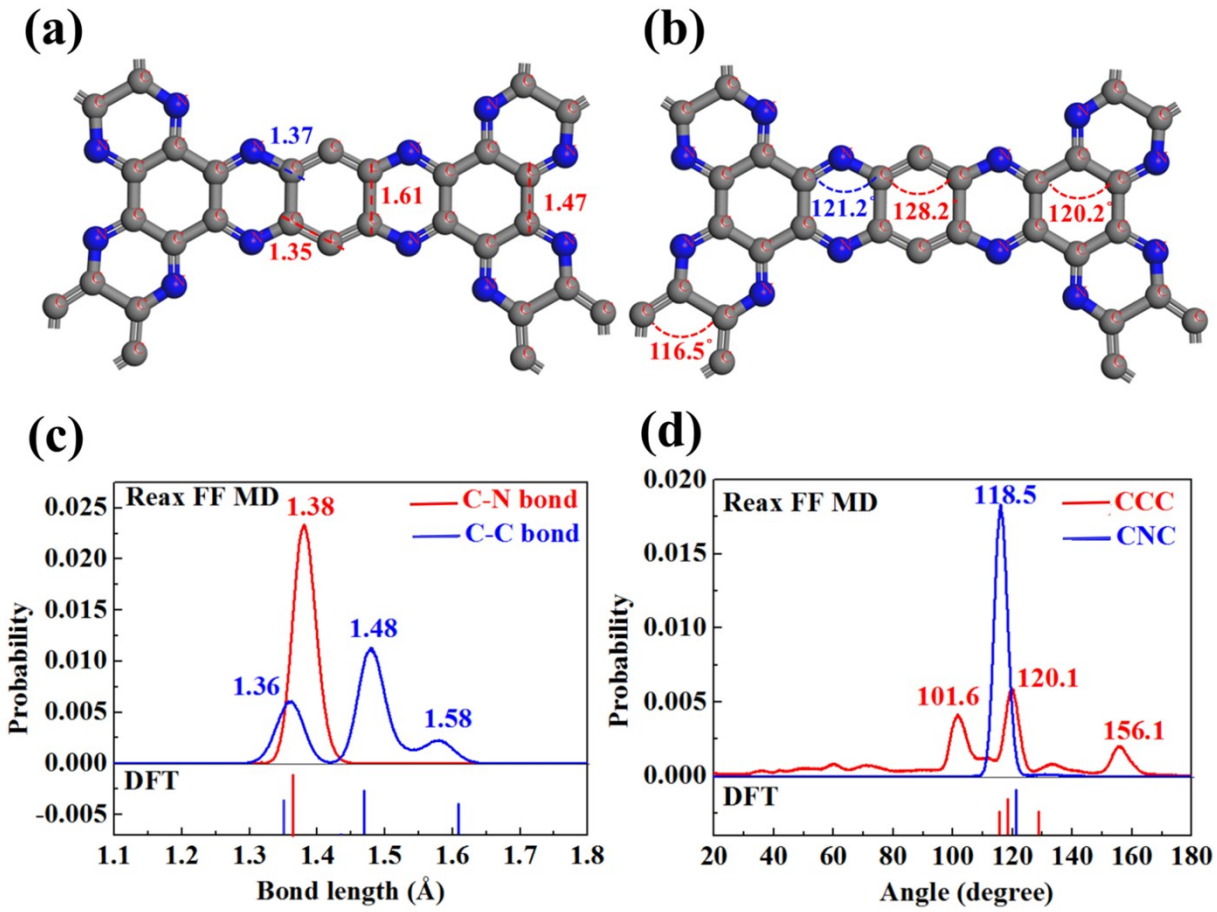

Fig. S1 Validate the C/N/O/H ReaxFF force field parameters. (a) (b) Optimized the bond length and angle of dehydrogenated g-C_5N_2 structure by *ab initio* density functional theory (DFT) calculation. (c) (d) Comparisons between DFT and RxMD results for calculating the bond length and angle distribution functions.

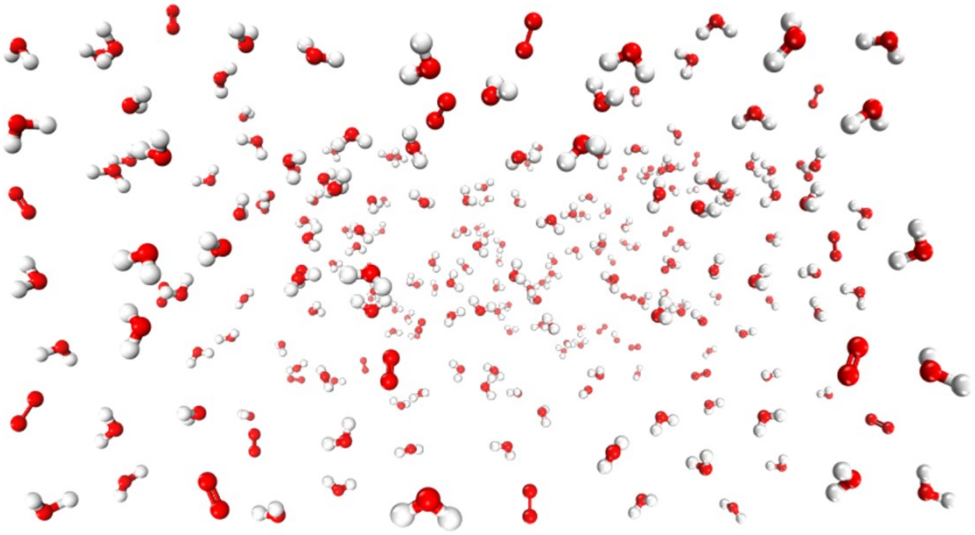

Fig. S2 Snapshot of H_2O and O_2 by the RxMD simulations at 5.0 ns.

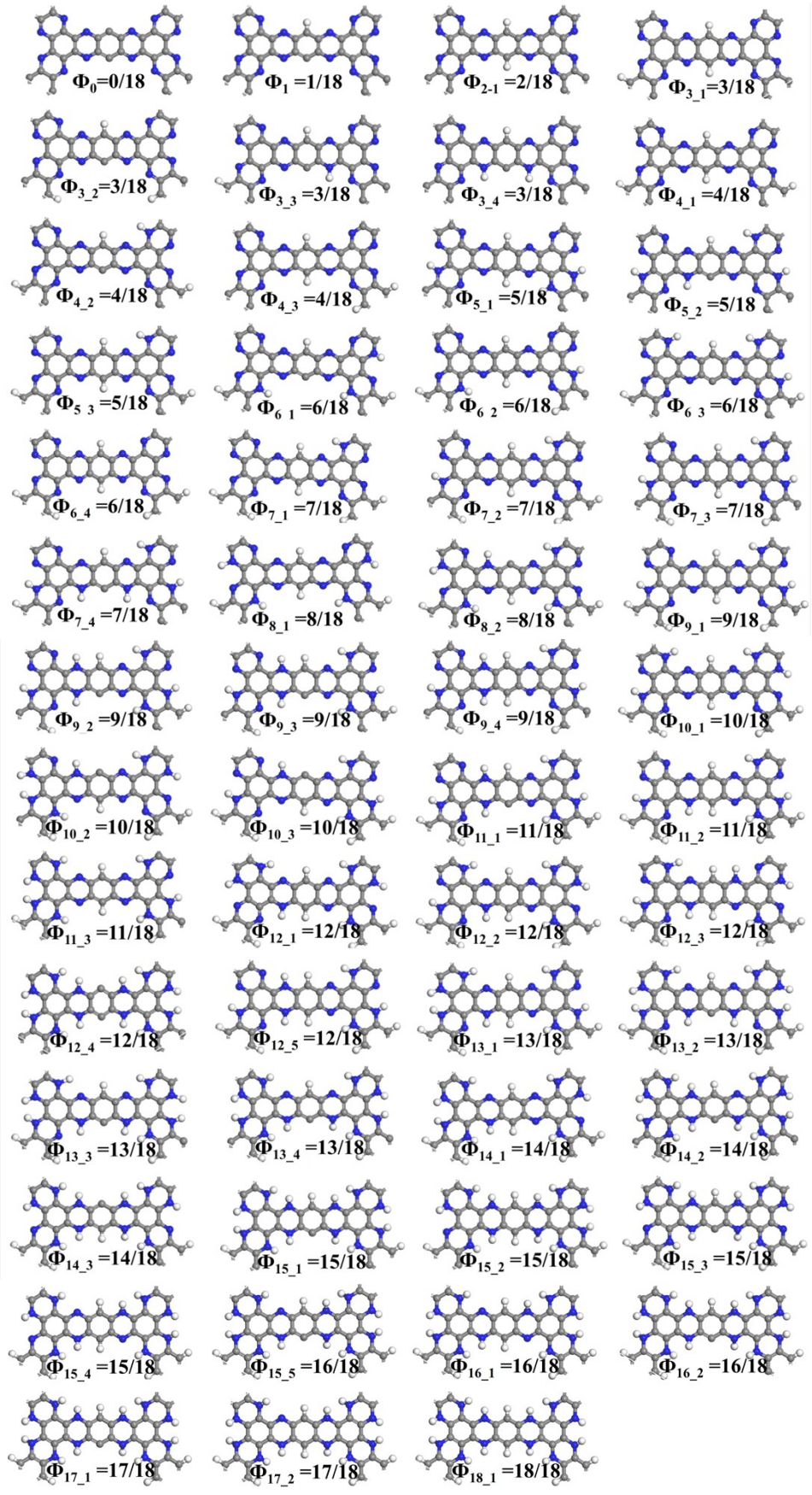

Fig. S3 The different the models of hydrogenation coverage of g-C_5N_2.

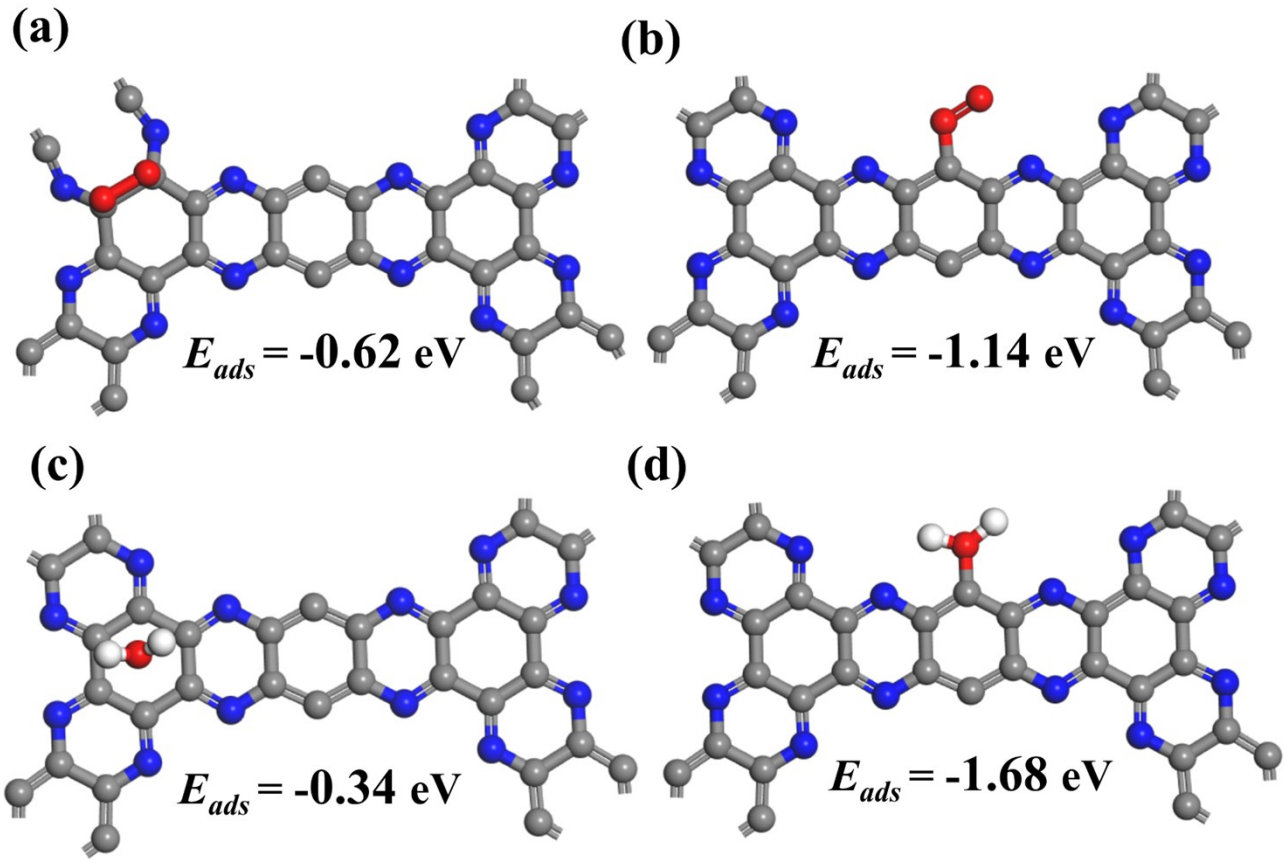

Fig. S4 Optimized configurations and adsorption energy for O_2 and H_2O binging on the basal plane (a, c) and the pore (b, d) of dehydrogenated g-C_5N_2, respectively.

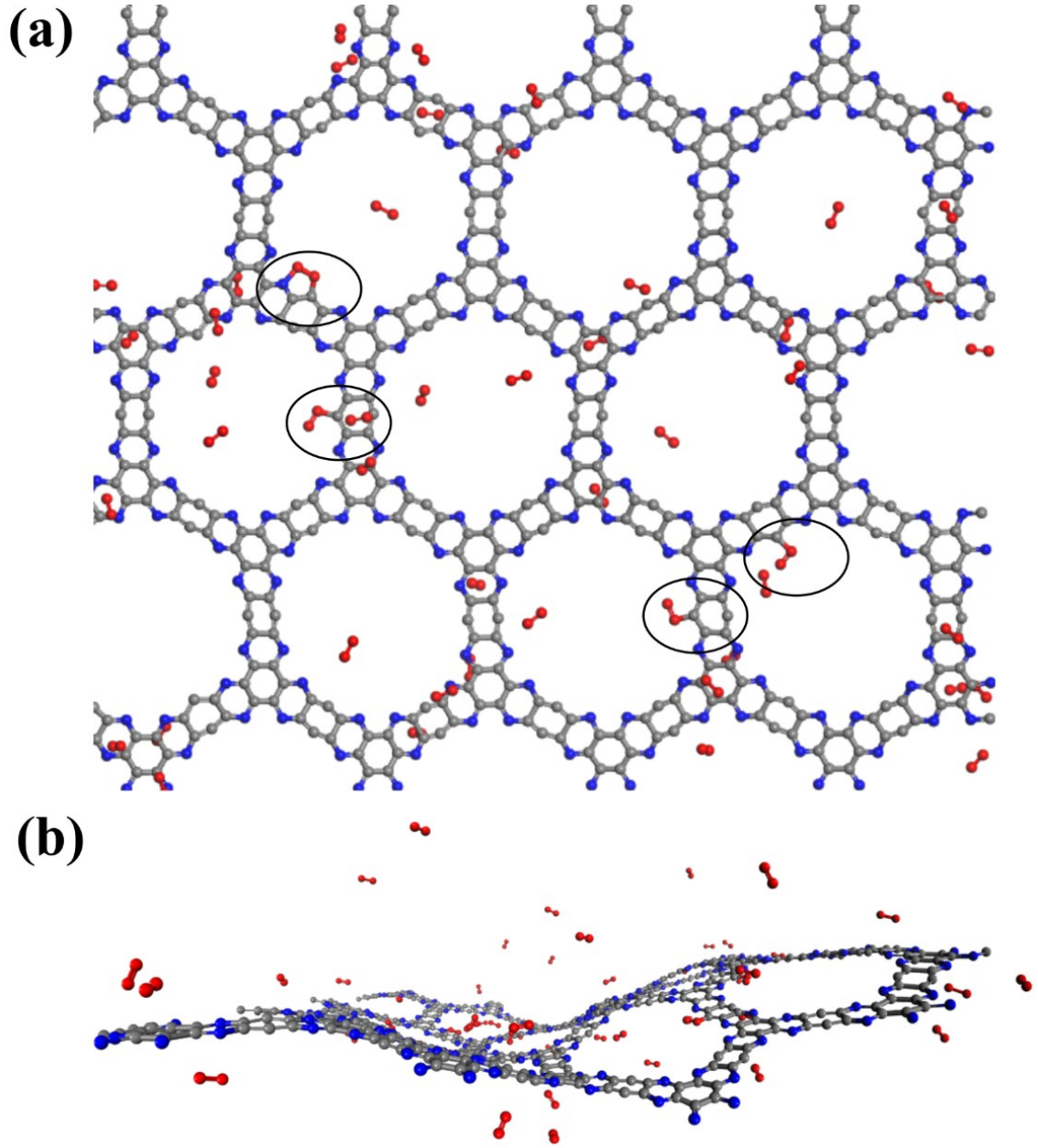

Fig. S5 (a) (b) the top and side view of configuration of the g-C_5N_2 with 50 O_2 molecules after 2.0 ns.

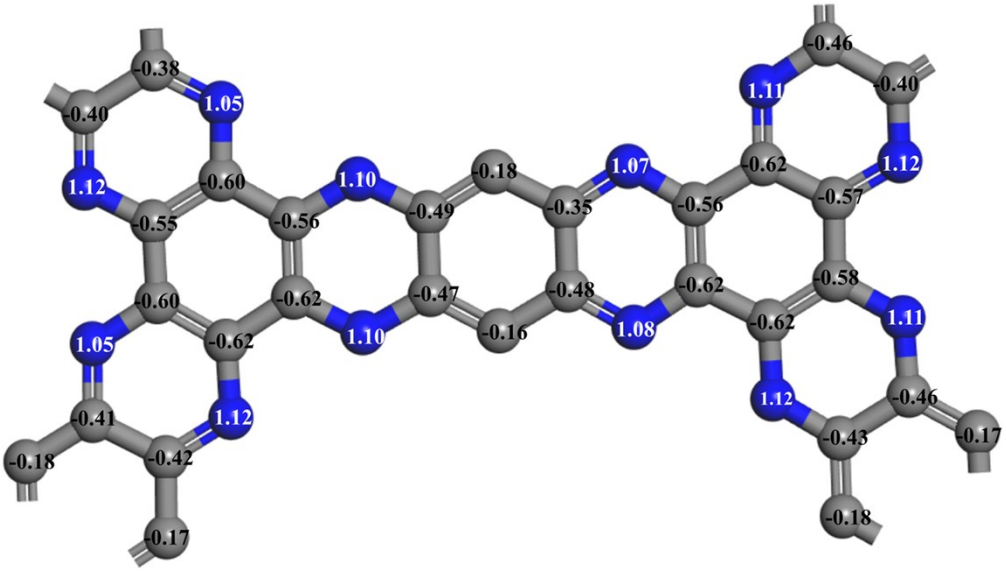

Fig. S6 Distribution of the Bader charge of dehydrogenated g-C_5N_2. The negative sign"-" represents the loss of electrons.

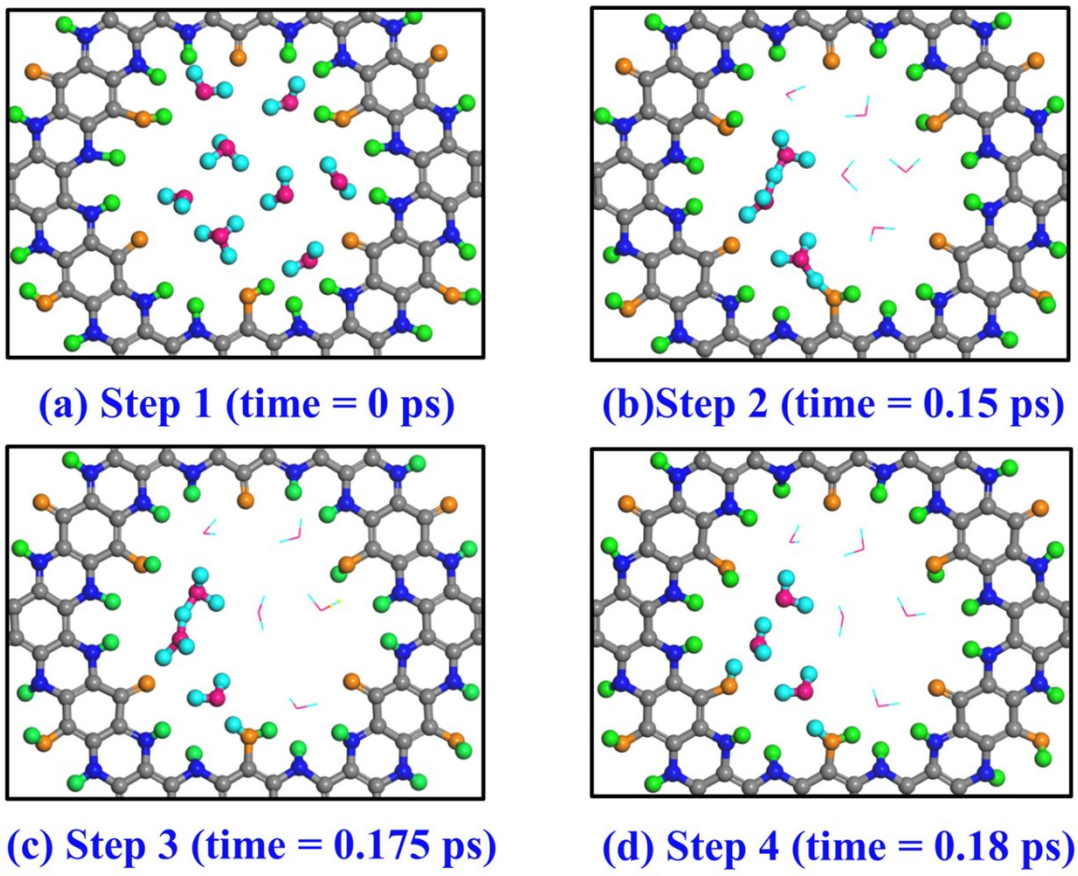

Fig. S7 Ab initio molecular dynamics calculation of g-C_5N_2 regeneration in an acid solution: 6 H_2O molecules and 2 H_3O^+ molecules are placed in the pore of a deactivated g-C_5N_2. Edge nitrogen sites are fully hydrogenated and carbon sites are alternatively bonded with OH and O, mimicking the accumulation of OH and O after H_2O_2 production. The color codes are: C of g-C_5N_2, gray; N of g-C_5N_2, blue; H of free H_2O, cyan; O of free H_2O, pink; H of adsorbed H_2O, green; O of adsorbed H_2O, yellow. Both line and ball models are used to illustrate the removal of adsorbed OH and O, and the regeneration of g-C_5N_2 catalyst.

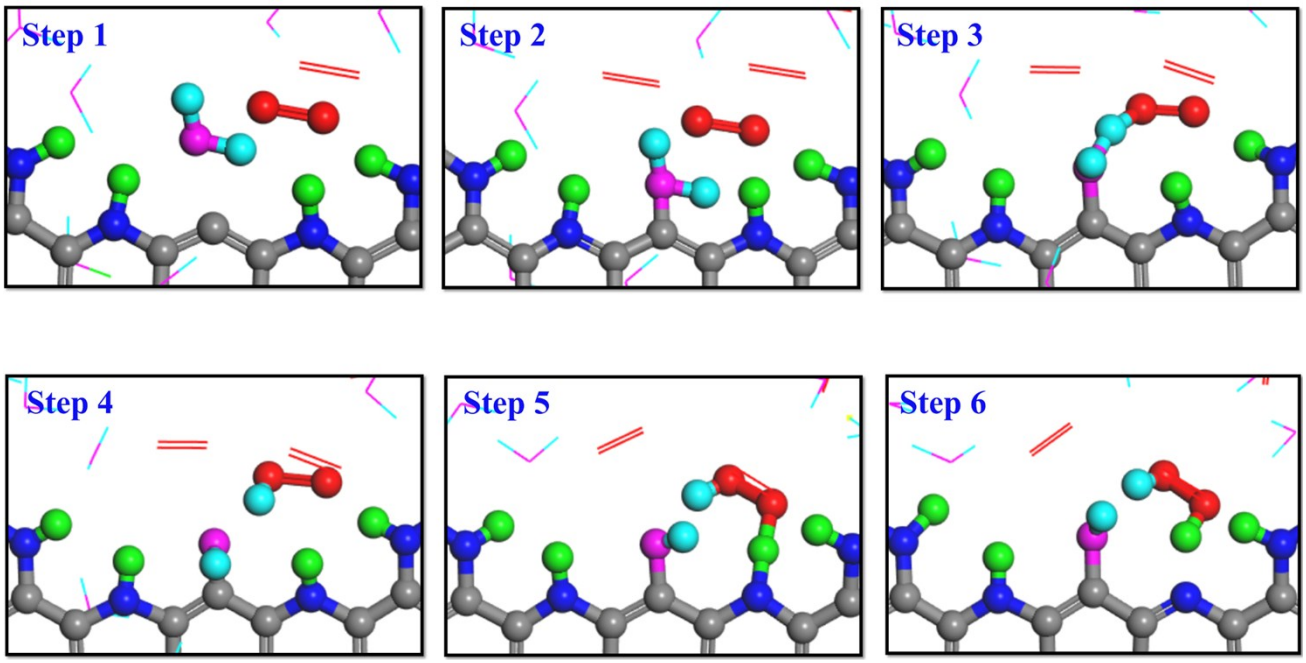

Fig. S8 Snapshots of H_2O_2 production on the N-site full hydrogenation g-C_5N_2 (Model 3) described by the AIMD simulations. The two hydrogen atoms of H_2O_2 come from the adsorbed H_2O and the N-site full hydrogenation g-C_5N_2. The color codes are: C of g-C_5N_2, gray; N of g-C_5N_2, blue; H of free H_2O, cyan; O of free H_2O, pink; H of adsorbed H_2O, green; O of adsorbed H_2O, red. Both line and ball models are used in the snapshots, to empahsize the formation of H_2O_2. For clarity, not all free water molecules are shown.

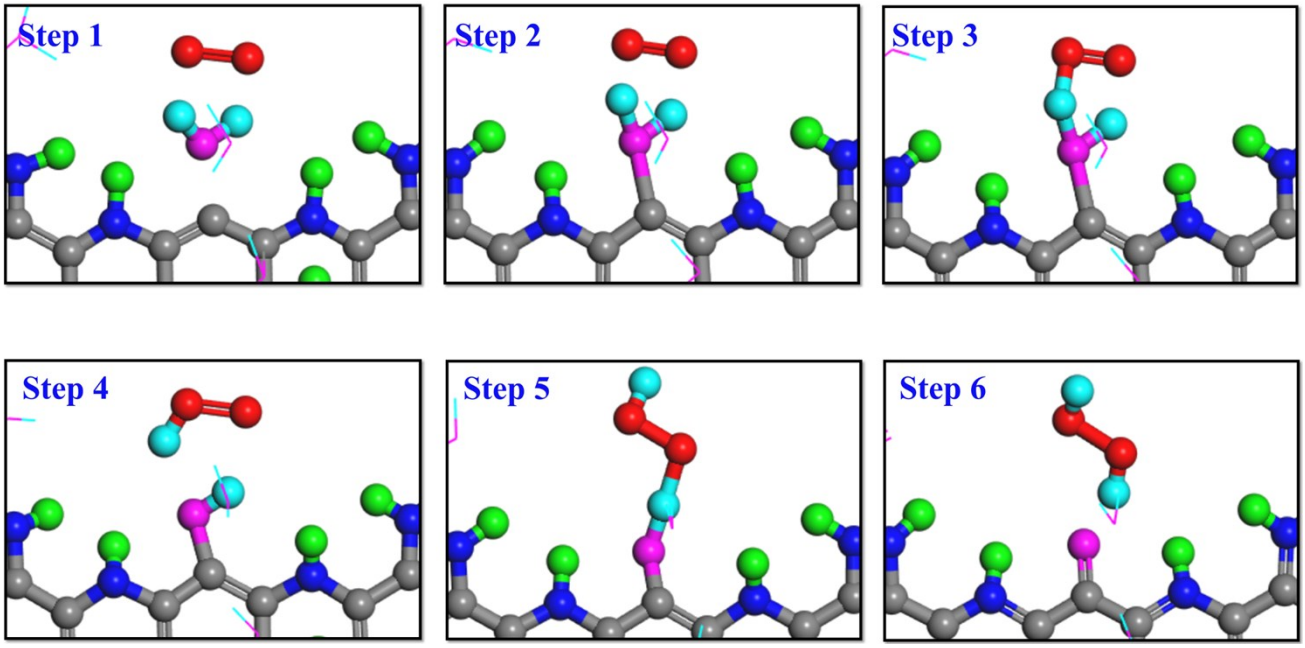

Fig. S9 Snapshots of H_2O_2 production on the N-site full hydrogenation g-C_5N_2 described by the AIMD simulations. The two hydrogen atoms of H_2O_2 come from the one adsorbed H_2O.

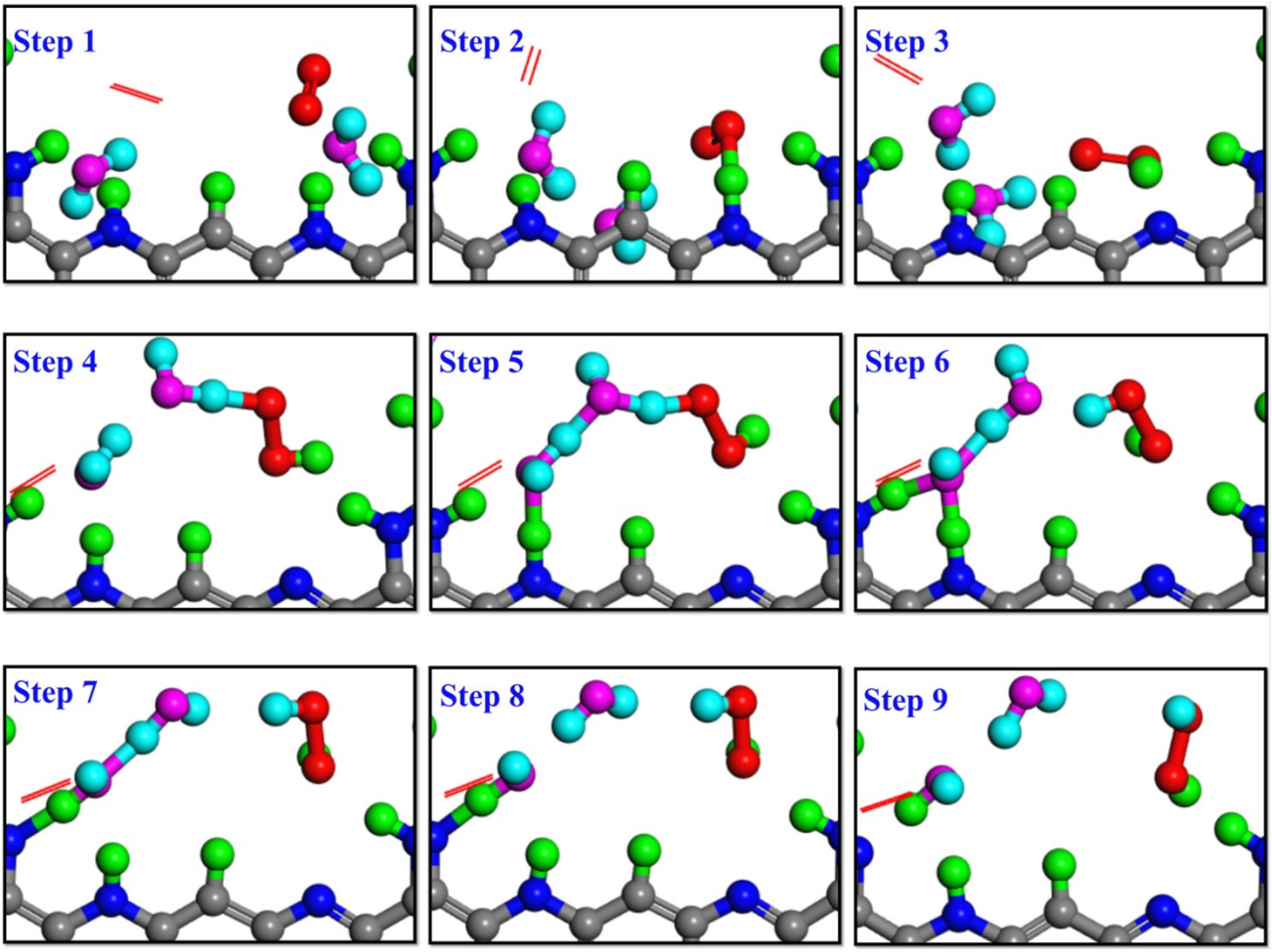

Fig. S10 Snapshots of H_2O_2 production on full hydrogenation g-C_5N_2 (Model 4) described by the AIMD simulations. Structures corresponding to the reaction path followed by PTM.

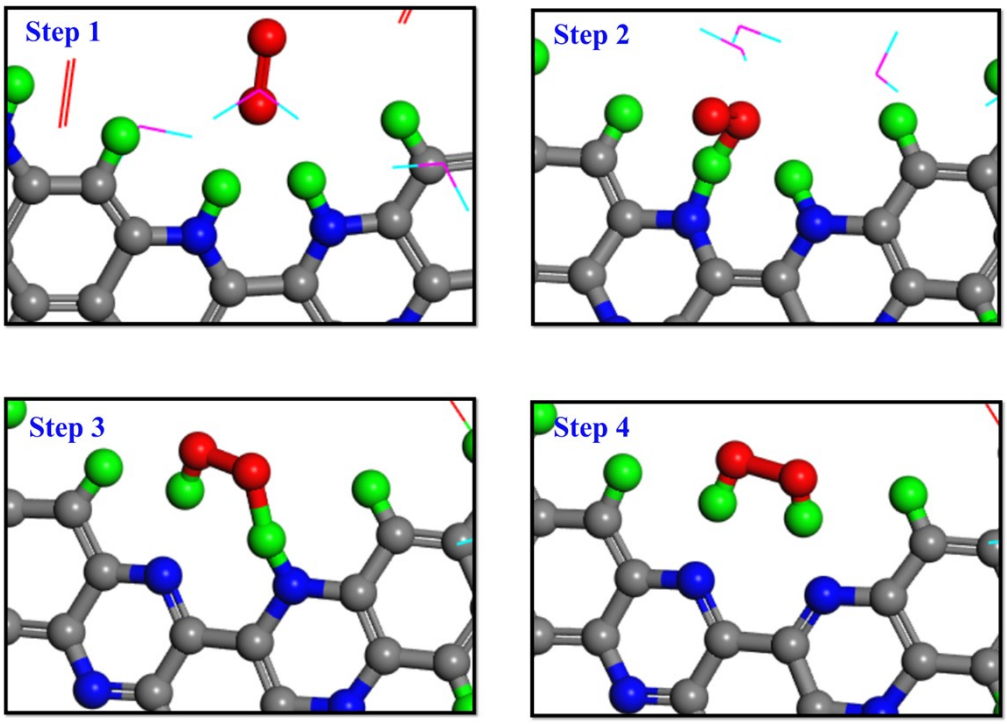

Fig. S11 Snapshots of H_2O_2 production on full hydrogenation g-C_5N_2 by the AIMD simulations.

Structures corresponding to the reaction path followed by DFM.

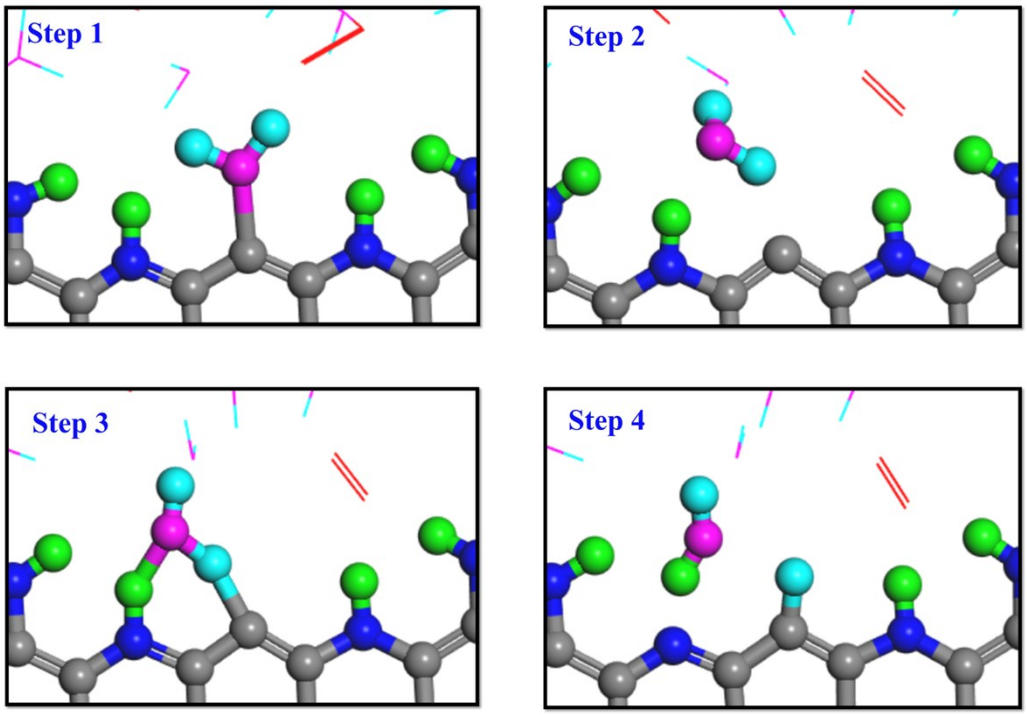

Fig. S12 Schematic representation of proton transfer between adsorbed H_2O molecules and N-site full hydrogenation g-C_5N_2.

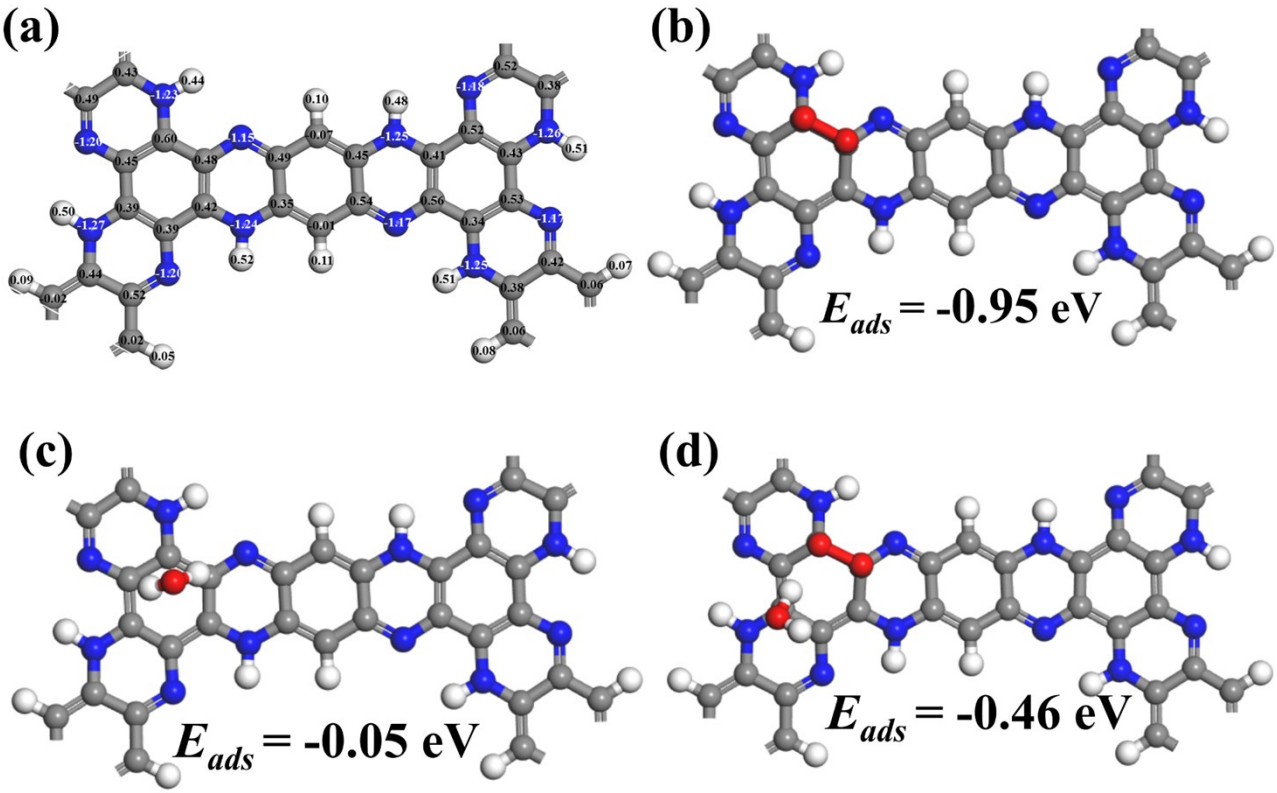

Fig. S13. (a) Distribution of the Bader charge of Model 5. Optimized configurations and adsorption energy for O_2 (b), H_2O (c), and O_2 and H_2O (d) binging on partially hydrogenation g-C_5N_2, respectively.

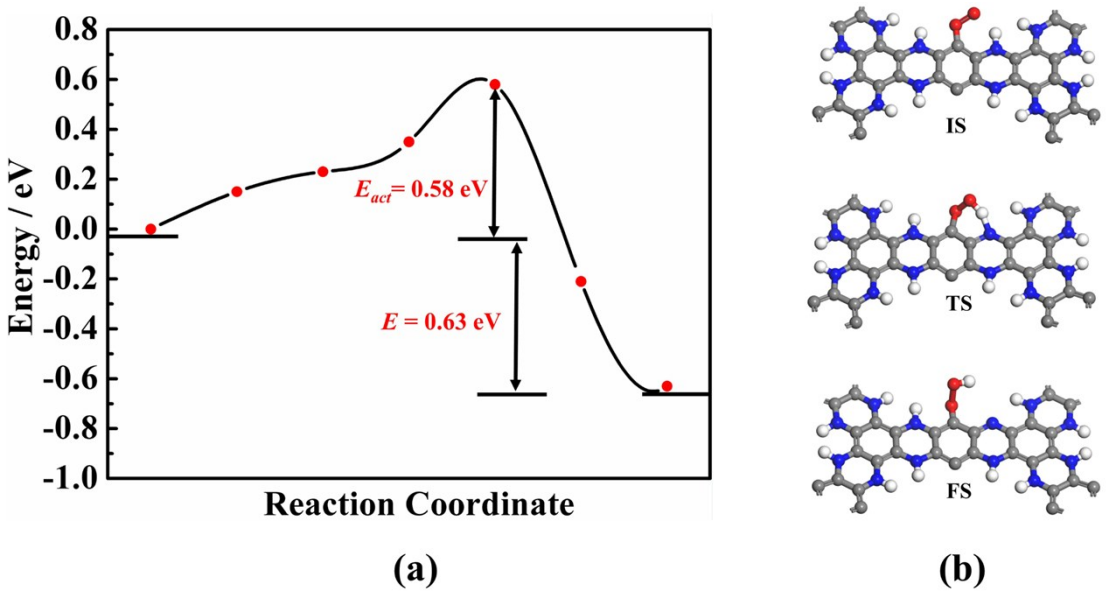

Fig. S14 (a), (b) Energy profile and optimized configurations for OOH* formation in the model 3.

Table S1 Variations in the energy for g-C_5N_2 under different hydrogen coverage by DFT calculation.

Coverage	Energy (eV)	Coverage	Energy (eV)
Φ_0=0/18	-351.41	Φ_{10_2}=10/18	-405.33
Φ_{1_1}=1/18	-357.52	Φ_{10_3}=10/18	-405.86
Φ_{2_1}=2/18	-364.06	Φ_{11_1}=11/18	-409.16
Φ_{3_1}=3/18	-369.97	Φ_{11_2}=11/18	-410.94
Φ_{3_2}=3/18	-369.37	Φ_{11_3}=11/18	-406.59
Φ_{3_3}=3/18	-368.58	Φ_{12_1}=12/18	-415.21
Φ_{3_4}=3/18	-368.01	Φ_{12_2}=12/18	-415.11
Φ_{4_1}=4/18	-375.87	Φ_{12_3}=12/18	-415.40
Φ_{4_2}=4/18	-373.72	Φ_{12_4}=12/18	-402.78
Φ_{4_3}=4/18	-376.46	Φ_{12_5}=12/18	-415.35
Φ_{5_1}=5/18	-379.04	Φ_{13_1}=13/18	-418.18
Φ_{5_2}=5/18	-379.14	Φ_{13_2}=13/18	-415.91
Φ_{5_3}=5/18	-380.27	Φ_{13_3}=13/18	-414.07
Φ_{6_1}=6/18	-383.47	Φ_{13_4}=13/18	-412.07
Φ_{6_2}=6/18	-385.21	Φ_{14_1}=14/18	-421.58
Φ_{6_3}=6/18	-382.42	Φ_{14_2}=14/18	-415.78
Φ_{6_4}=6/18	-388.89	Φ_{14_3}=14/18	-417.70
Φ_{7_1}=7/18	-393.33	Φ_{15_1}=15/18	-419.07
Φ_{7_2}=7/18	-391.82	Φ_{15_2}=15/18	-421.12
Φ_{7_3}=7/18	-389.95	Φ_{15_3}=15/18	-422.96
Φ_{7_4}=7/18	-386.77	Φ_{15_4}=15/18	-424.94
Φ_{8_1}=8/18	-394.72	Φ_{16_1}=16/18	-428.51
Φ_{8_2}=8/18	-392.52	Φ_{16_2}=16/18	-426.63
Φ_{9_1}=9/18	-402.17	Φ_{16_3}=16/18	-424.41
Φ_{9_2}=9/18	-397.05	Φ_{17_1}=17/18	-429.81
Φ_{9_3}=9/18	-400.20	Φ_{17_2}=17/18	-431.72
Φ_{9_4}=9/18	-398.93	Φ_{18_1}=18/18	-434.29
Φ_{10_1}=10/18	-406.59		

Table S2 Gibbs free energy variations as a function of temperature for gaseous hydrogen at standard state pressure, P^0 = 1.0 atm. Data are taken from the NIST thermodynamic tables.

T/K	$\Delta G^{gas}_{H_2}$(T, P^0)/ eV	T/K	$\Delta G^{gas}_{H_2}$(T, P^0)/ eV
298.15	0.00	700	-0.58
300	-0.003	800	-0.74
400	-0.14	900	-0.90
500	-0.28	1000	-1.07
600	-0.43	1100	-1.23

Table S3 The Gibbs free energy variations as a function of temperature for gaseous oxygen at standard state pressure, P^0 = 1.0 atm with respect to its value at 0.0 K.

T/K	$\Delta G^{gas}_{H_2}(T, P^0)$/ eV	T/K	$\Delta G^{gas}_{H_2}(T, P^0)$/ eV
298.15	-0.27	700	-0.85
300	-0.41	800	-1.01
400	-0.14	900	-1.17
500	-0.55	1000	-1.34
600	-0.70	1100	-1.50