Electronic Supplementary Material (ESI) for Nanoscale.

Supplementary Information for

Photocatalytic Activity of Dual Defect Modified Graphitic Carbon Nitride is Robust to Tautomerism: Machine Learning Assisted Ab Initio Quantum Dynamics

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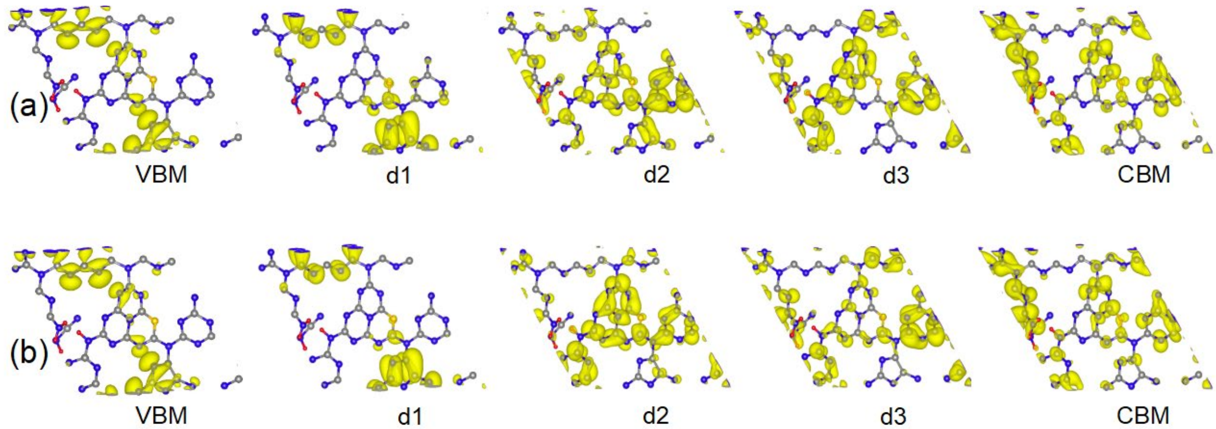

Figure S1. Charge densities of the key KS orbitals in the active space for **(a)** spin up **(b)** spin down channels of the most stable structure (NH-CN) of ON-GCN. The CBM is delocalized over the whole system including the defect region containing the N and O defects, while the VBM is localized over the region away from the defect centers. The d1 trap state is localized on the tri-s-triazine unit containing a C−C bond resulting from the N-vacancy defect. The d2 and d3 trap states are mostly localized on the tri-s-triazine unit containing the other defect (CN group). The O-defect has little influence on the charge density of both band edges and the defect states.

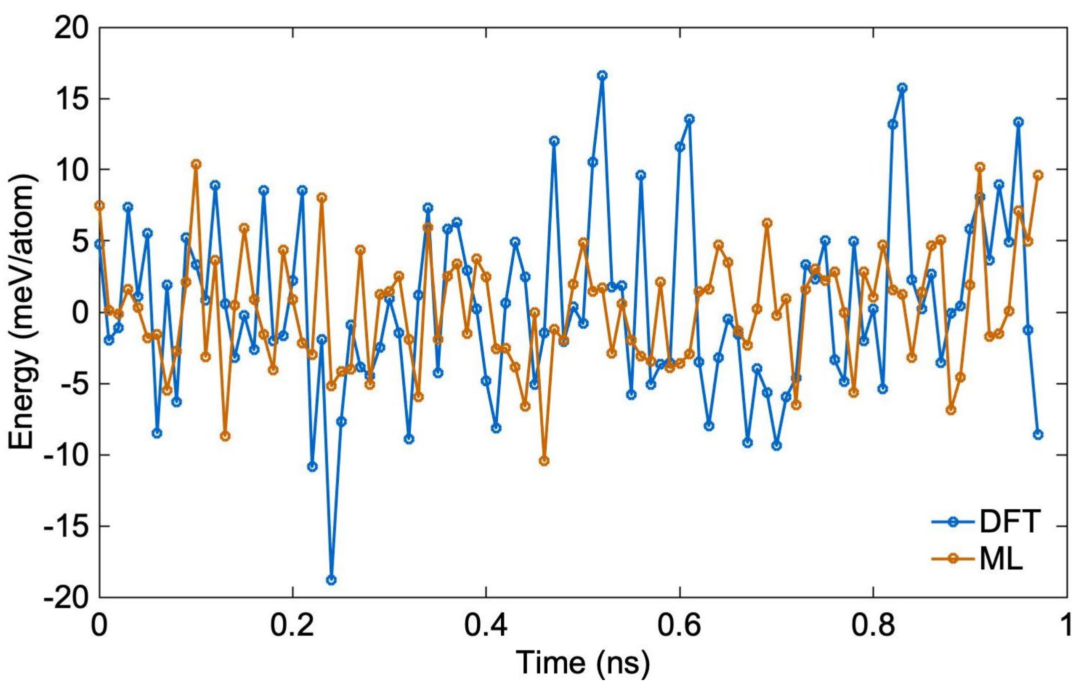

Figure S2. Comparison of ML and DFT potential energies for the trajectory obtained starting from the N*H*-CN (most stable) structure. The total energies plotted are subtracted from the mean values for both the cases. The root-mean-square error is 7.27 meV/atom.

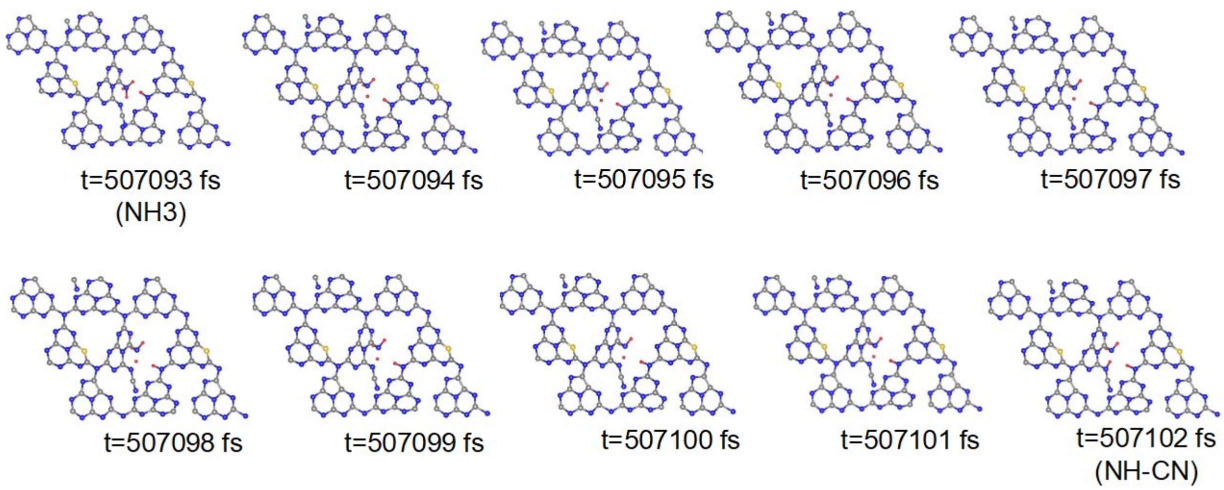

Figure S3. Snapshots of a representative hydrogen hopping dynamics. In this example it takes 9 fs for the hydrogen to hop from NH_3 to the NH-CN structure.

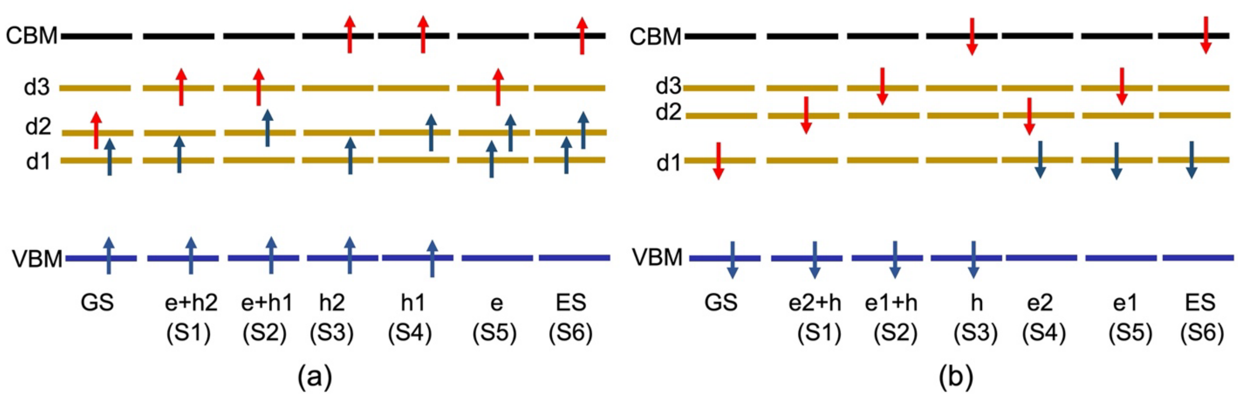

Figure S4. Schematic of the electronic configurations in the active space used to model charge carrier trapping and recombination in **(a)** ON-gcn (spin-up), and **(b)** ON-gcn (spin-down).

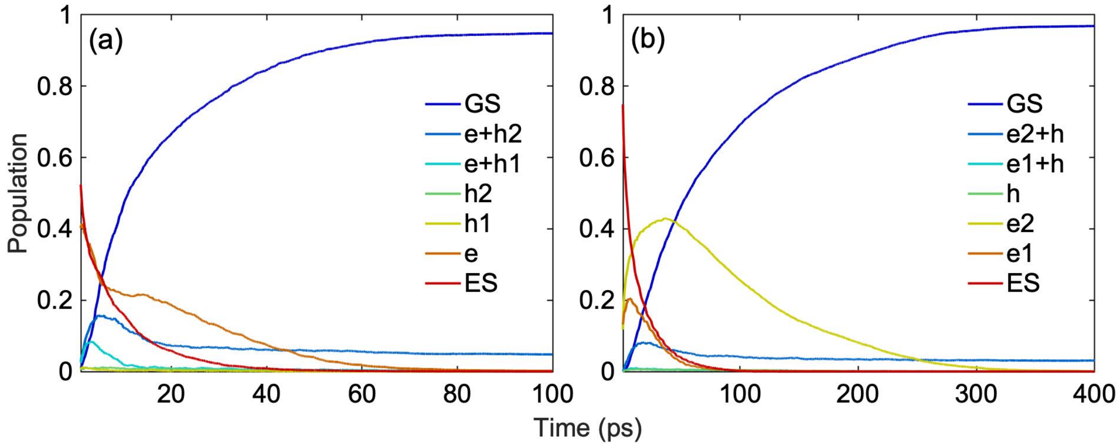

Figure S5. Nonradiative charge trapping and recombination dynamics in **(a)** spin up **(b)** spin down channels of the most stable tautomer (NH-CN) of ON-GCN (Figure 1a). The corresponding timescales are given in Table S1. Abbreviations used: GS- ground state, ES- initial excited state, e- electron trap, h- hole trap. The legends used here correspond to the electronic configurations labeled in Figure S4.

Table S1. Nonradiative timescales (in ps) for the rise and decay of populations of the states in the active space, Figure S4. Charge trapping and recombination are faster in the spin up channel compared to the spin down channel.

	GS	**S1**		**S2**		**S3**		**S4**		**S5**		**S6**
	rise	rise	decay	rise	decay	rise	decay	rise	decay	rise	decay	decay
Spin up	20.47	3.12	7.43	1.73	3.44	0.45	25.3	0.49	25.06	0.19, 2.76	2.57, 155.01	1.09
Spin down	76.28	20.83	28.29	8.74	90.33	11.66	109.6	3.04, 156	52.19	0.43, 16.2	32.15	19.13

Optimized structure of the most stable NH-CN tautomer in the VASP POSCAR format.

```
g-C3N4 monolayer
   1.00000000000000
    13.6378442312651984    0.4991236984113793   -0.0265390736764531
    -6.9789988076018243   10.9961164586099009   -0.5100408234215591
     1.1547517345598848   -2.7312477911448041   22.9706408144469592
   C    N    O    H
    24    31     1     4
Direct
  0.1472645560445457  0.0917115763374162  0.5573897344415477
  0.1092220637816272  0.5469700730608444  0.4435657529812784
  0.6021058748192891  0.0895772606788872  0.4678634329917011
  0.6276551007002864  0.5830568262137310  0.4665549433562126
  0.1668721029383204  0.2729965839450208  0.5705082906747999
  0.1040879275486402  0.7055214265495390  0.5010719676693033
  0.5837072465095807  0.1742039611473184  0.4413110237853344
  0.6431034706114558  0.7645875808596243  0.5020565329881280
  0.9054015942146629  0.1514056112726134  0.4140156647315237
  0.1145291944465202  0.8981628139703516  0.5337621725547934
  0.5993191319165253  0.3795218305874562  0.4502590046861795
  0.6347883336085119  0.9608113966321108  0.5080225039913321
  0.3322910753501186  0.4423725368814664  0.5435403222819055
  0.2780613758565595  0.8961603275026374  0.4978613598030198
  0.7668288046191729  0.3599883333771844  0.4460005829820021
  0.8125949822478047  0.9514725706792565  0.5248313387343082
  0.4535547293890557  0.4056565864294358  0.4864372868448642
  0.4550226181257013  0.9255294994492029  0.5100971698757720
  0.9271014894677883  0.3440254660350763  0.4341957777005863
  0.9562506988831531  0.9220763077822618  0.5390726831242054
  0.4117129950210974  0.0293444637815795  0.4495755541654608
  0.4921238954503357  0.6059815254489519  0.5300934531436715
  0.9848042500967151  0.1242032169144450  0.5464509381313016
  0.9342357316711101  0.5273830791114380  0.4848651415754075
  0.0304350793842352  0.0470789894756196  0.5507805584089823
  0.9927137123820122  0.4698750721599653  0.4496849862648423
```

0.4876055992743632	0.0035560678319546	0.4725164922617869
0.5266435717099357	0.5326382289739338	0.4914113079180502
0.0555567786317937	0.2418119633618667	0.5594195150560435
0.9997909475170907	0.6398238637490237	0.5170944284078834
0.4698322831247969	0.1252580771685128	0.4261264195587061
0.5646015305025839	0.7243436785594666	0.5399238286565112
0.4966373187971113	0.3351873065230166	0.4648719461736037
0.5310981262062116	0.8984090947827484	0.5302866814837960
0.9709405930715762	0.2668052893352109	0.4398203049110215
0.9985423000649306	0.8440823246846156	0.5296824104514860
0.1883412919904676	0.0151110365100323	0.5506013128107548
0.8521012000840895	0.0497731872900176	0.3914328877755931
0.6784445669963846	0.0588014178678363	0.4848689178653557
0.2377177233772920	0.3963383130892822	0.5730368558030915
0.1636294461977515	0.8296231254115625	0.5172872681624859
0.6479895205212025	0.3031307789307838	0.4383866594144508
0.7014686261108066	0.8963612337478901	0.5081829278435285
0.3943720353955950	0.5658843676489811	0.5534411772346515
0.2956565931100794	0.9633379998503114	0.4579183637357290
0.8228774841603420	0.4692902994740081	0.4790200088258910
0.8782604264538522	0.0721619422071974	0.5287210744662365
0.2148925330681490	0.2074222084146750	0.5714582558475566
0.1661513012832710	0.6661246555654429	0.4641754470355717
0.6822808093198346	0.7026888932649964	0.4652315509099562
0.3537192680297553	0.3660101156003034	0.5083167581342221
0.3517771157924462	0.8853874515828796	0.5299261338680356
0.8144186649502698	0.2925730614279604	0.4312244441122204
0.8467605549596812	0.8763517415085881	0.5364905034492771
0.1660257735630066	0.4979030838629696	0.4143246431848363
0.6663743137463335	0.5041451861242886	0.4435951752970953
0.2179256807513179	0.4531171969787575	0.5971094593517330
0.1225291693379864	0.4154561656656488	0.3886104196866857
0.2512826409073943	0.5502786620820556	0.4089685245591433
0.0032064118473669	0.2703334565603763	0.4824572720649541