Electronic Supplementary Information

Site-Dependent Photoinduced Charge Carrier Dynamics in Nitrogen/Fluorine Doped TiO_2 Nanoparticles

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Table S1. Formation energies (E_f^0) and defect energy levels (HT3, ET) in the doped TiO_2 nanoparticles. The numbers in HT3/ET shows the energy gap between HT3/ET and VBM/CBM, respectively.

Type of doping	N-doping			F-doping	
	E_f^0 (eV)	HT1 (eV)	HT2 (eV)	E_f^0 (eV)	ET
T1-1	3.034	1.578 (HT2)	1.389 (HT3)	0.156	0.819
E2-1	3.069	0.671	0.997	0.933	1.216
E2-2	3.053	0.532	1.164	0.859	1.394
E2-3	3.116	0.709	0.972	0.928	1.147
E2-4	3.060	0.759	0.867	0.789	1.234
E2-5	2.830	0.674	0.707	0.630	1.298
E2-6	2.816	0.773	0.664	0.589	1.400
E2-7	2.915	0.563	0.590	0.907	1.044
F2-1	2.898	0.579	0.816	0.950	0.900
F2-2	2.866	0.454	0.685	1.040	0.553
F2-3	2.721	0.380	0.815	1.154	1.376
F3-1	2.736	0.407	1.124	1.324	1.258
F3-2	2.796	0.471	1.203	1.357	1.393
F3-3	2.721	0.385	1.074	1.226	0.881
F3-4	2.805	0.372	1.141	1.592	0.708
F3-5	2.752	0.493	1.198	1.575	1.173
F3-6	2.806	0.426	1.077	1.450	1.250
F3-7	2.797	0.415	1.037	1.371	1.478
F3-8	2.870	0.415	1.200	1.112	1.042
F3-9	2.595	0.385	0.693	1.008	1.496
F3-10	2.659	0.349	1.119	2.222	0.824
I3-1	2.749	0.567	0.768	1.079	0.628
I3-2	2.846	0.364	1.292	1.740	1.030
I3-3	2.899	0.377	1.441	1.822	0.991
I3-4	2.973	0.354	1.556	2.127	0.479

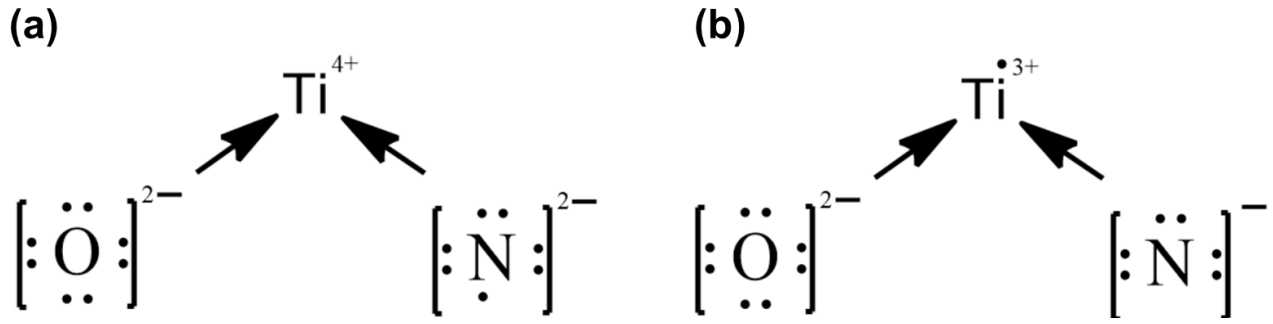

Figure S1. Lewis dot structure for TiON.

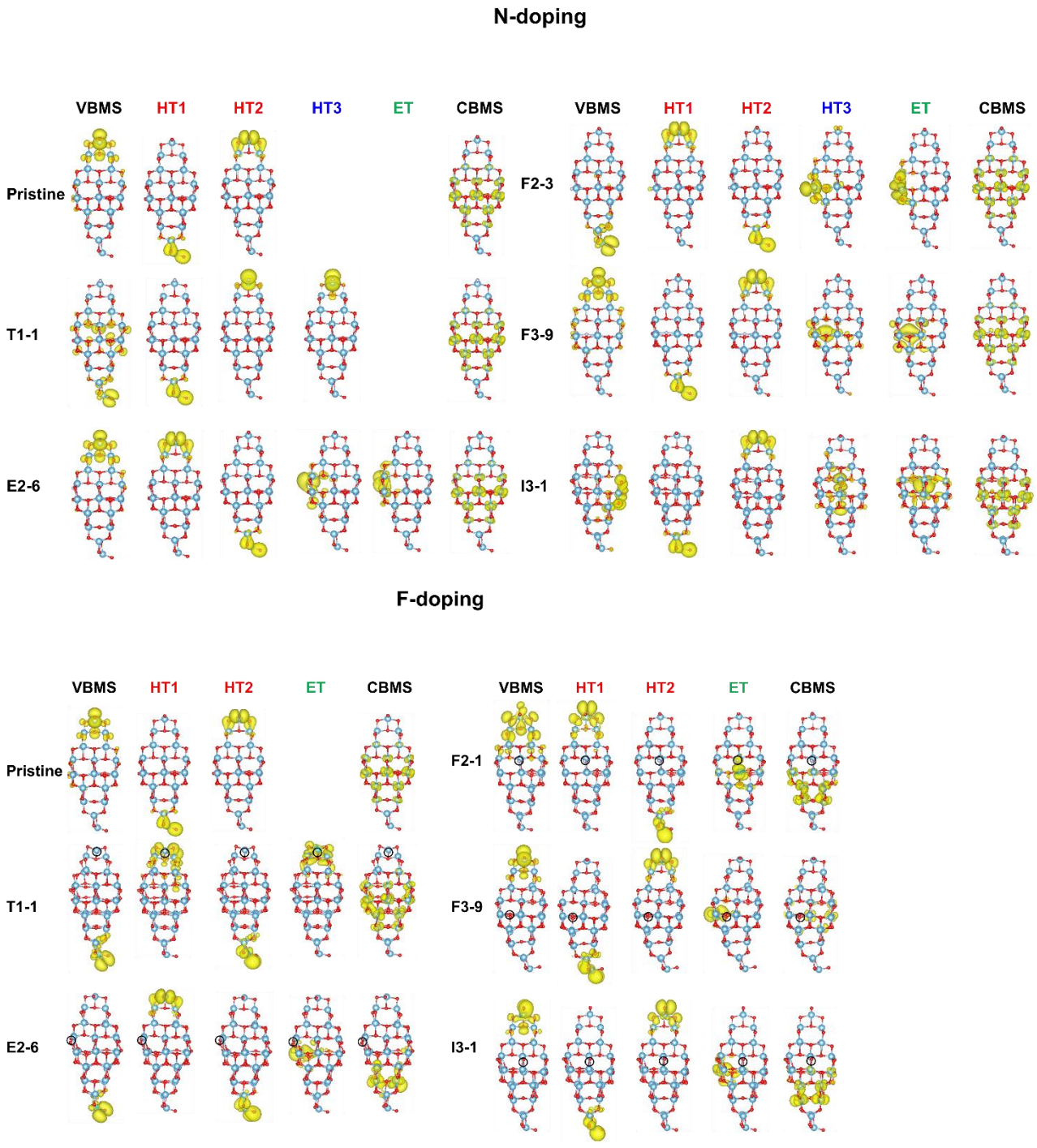

Figure S2. Charge densities of VBMS to CBMS in the N- or F-doped TiO_2 nanoparticles. The isosurface value is 0.001 e au^{-3}. The doping sites are marked with black circles.

Table S2. Fitting parameters (C, A, and t) for time evolution of populations of the key states.

N-doping	Ex			S7						S6						S5					
	C	A	t (fs)	C	A	t (fs)	C	A	t (fs)	C	A	t (fs)	C	A	t (fs)	C	A	t (fs)	C	A	t (fs)
Pristine							0.002	1.127	80.631	0.296	-0.323	53.581	0.009	0.527	149.366	0.260	-0.289	118.117	0.056	0.373	302.874
T1-1	0.023	1.094	136.230	0.542	-0.605	124.663	0.088	0.532	393.678												
E2-6	0.001	1.123	69.543	0.320	-0.347	46.920	0.004	0.330	244.837	0.471	-0.540	82.151	0.021	0.472	1003.065	0.559	-0.592	227.157	0.011	0.753	2405.735
F2-3	0.004	1.073	82.732	0.271	-0.293	41.826	0.013	0.362	210.110	0.407	-0.464	72.080	0.101	0.182	2666.730	0.699	-0.811	212.855	-0.007	0.765	12217.559
F3-9	0.000	1.099	80.909	0.265	-0.278	44.956	0.004	0.366	180.509	0.373	-0.419	85.471	0.012	0.276	1761.060	0.686	-0.766	208.265	0.004	0.782	2688.016
I3-1	0.003	1.081	90.413	0.342	-0.374	50.336	0.019	0.434	258.600	0.547	-0.606	121.503	0.095	0.245	3061.965	0.649	-0.755	319.639	0.020	0.665	8996.749

F-doping	Ex			S5						S4					
	C	A	t (fs)	C	A	t (fs)	C	A	t (fs)	C	A	t (fs)	C	A	t (fs)
Pristine	0.002	1.127	80.631	0.296	-0.323	53.581	0.009	0.527	149.366	0.260	-0.289	118.117	0.056	0.373	302.874
T1-1	0.034	1.093	86.461	0.541	-0.585	79.415	0.182	0.427	190.771	0.776	-0.913	155.194			
E2-6	0.010	1.065	113.209	0.381	-0.420	67.529	0.047	0.209	1632.350	0.750	-0.820	191.667	-0.002	0.848	6346.038
F2-1	0.040	1.018	107.369	0.416	-0.450	-70.780	0.205	0.316	439.270	0.733	-0.724	-260.783	0.090	0.630	39232.025
F3-9	0.020	1.061	104.695	0.413	-0.449	-70.097	0.119	0.554	214.744	0.849	-0.942	-196.764	0.711	0.150	11689.201
I3-1	0.017	1.106	90.684	0.444	-0.477	85.022	0.128	0.273	304.636	0.827	-0.928	152.346	0.285	0.553	25515.292

Table S3. Average transition energies (T.E.), absolute nonadiabatic coupling (NAC), pure-dephasing times (Dephasing) and nonradiative trapping/recombination times (Time), where the electron trapping was calculated for LUMO to ET transition only and electron-hole recombination for ET to HT3 only. Note that N-doped T1-1 does not have electron trapping and F-doped T1-1 has dual channel electron-hole recombination pathway.

N-doping	Hole trapping				Electron trapping	Electron-hole recombination
	S8 to S7	S7 to S6	S6 to S5	Total hole trapping time	S5 to S1	S1 to GS

	NAC (meV)	T.E. (eV)	Time (ps)	NAC (meV)	T.E. (eV)	Time (ps)	NAC (meV)	T.E. (eV)	Time (ps)		NAC (meV)	T.E. (eV)	Time (ps)	NAC (meV)	T.E. (eV)	Time (ps)
Pristine				44.581	0.128	0.134	24.382	0.204	0.267	0.402	20.450	0.121	0.258	2.247	2.303	118.789
T1-1	28.036	0.195	0.261							0.261			0.413	0.631	2.440	873.553
E2-6	47.418	0.118	0.116	27.918	0.186	0.327	18.027	0.287	1.230	1.674	7.386	0.671	3.015	2.824	1.419	320.136
F2-3	56.429	0.097	0.125	35.509	0.130	0.282	22.892	0.192	2.880	3.286	4.484	0.935	13.983	1.424	1.323	512.264
F3-9	61.411	0.093	0.126	39.413	0.153	0.266	28.834	0.193	1.969	2.361	8.925	0.758	2.975	0.841	1.530	1057.807
I3-1	41.528	0.095	0.141	26.92	0.158	0.380	14.513	0.247	3.382	3.902	4.926	0.703	9.597	1.831	1.513	1016.100

F-doping	Hole trapping							Electron trapping			Electron-hole recombination		
	S6 to S5			S5 to S4			Total hole Trapping time	S4 to S1			S1 to GS		
	NAC (meV)	T.E. (eV)	Time (ps)	NAC (meV)	T.E. (eV)	Time (ps)		NAC (meV)	T.E. (eV)	Time (ps)	NAC (meV)	T.E. (eV)	Time (ps)
Pristine	44.581	0.128	0.134	24.382	0.204	0.267	0.402	20.450	0.121	0.258	2.247	2.303	267.317
T1-1	44.820	0.115	0.166	25.300	0.180	0.346	0.512	0.619	1.245	712.520	0.732	1.204	133.708
											0.642	2.449	1130.645
E2-6	45.177	0.110	0.181	25.132	0.211	1.824	2.005	4.172	1.379	15.084	2.444	0.968	2.191
F2-1	32.409	0.118	0.178	20.891	0.178	0.700	0.878	2.049	0.898	52.938	0.275	1.511	13268.635
F3-9	53.038	0.132	0.175	25.782	0.246	0.412	0.586	3.381	1.543	116.886	1.426	0.743	2.635
I3-1	41.598	0.116	0.176	20.253	0.211	0.457	0.633	2.249	1.173	91.306	0.523	1.191	503.261

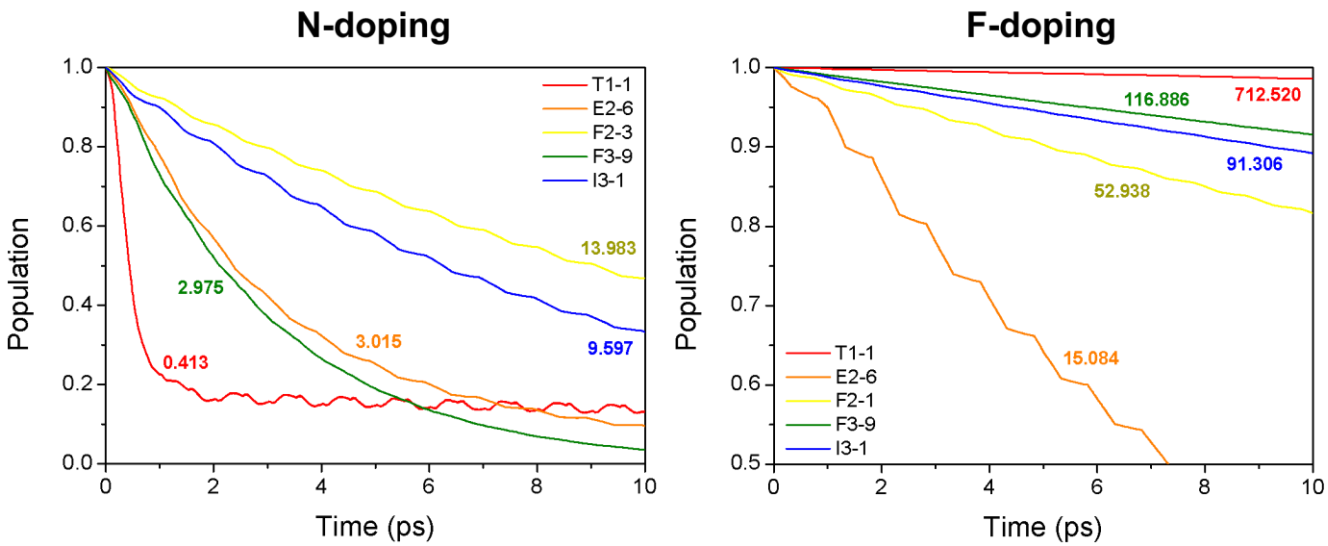

Figure S3. The electron trapping dynamics from CBM to ET state for N-doped and F-doped TiO_2 NPs.

Table S4. Average absolute nonadiabatic coupling for the charge carrier dynamics. The forbidden charge transitions are left as blanks.

Pristine

Pristine	GS	S1	S2	S3	S4	S5
S1	2.247					
S2	1.907	24.382				
S3	1.754	6.271	44.581			
S4	1.561	20.45				
S5	1.64		20.45		24.382	
Ex	1.579			20.45	6.271	44.581

N-doping

T1-1	GS	S1	S2	S3	S4	S5	S6	S7
S1	0.290							
S2	0.369	10.163						
S3	0.631	0.058	0.106					
S4	0.874	0.142	0.270	28.036				
S5	0.499	17.421						
S6	0.655		17.421			10.163		
S7	0.804			17.421		0.058	0.106	
Ex	0.924				17.421	0.142	0.270	28.036

E2-6	GS	S1	S2	S3	S4	S5	S6	S7
S1	2.824							
S2	1.005	18.027						
S3	0.554	3.335	27.918					

S4	0.565	1.576	5.023	47.418				
S5	2.434	7.386						
S6	0.983		7.386			18.027		
S7	0.831			7.386		3.335	27.918	
Ex	0.908				7.386	1.576	5.023	47.418

F2-3	GS	S1	S2	S3	S4	S5	S6	S7
S1	1.424							
S2	1.103	22.892						
S3	0.839	3.236	35.509					
S4	0.693	1.788	7.182	56.429				
S5	1.236	4.484						
S6	1.286		4.484			22.892		
S7	1.199			4.484		3.236	35.509	
Ex	1.185				4.484	1.788	7.182	56.429

F3-9	GS	S1	S2	S3	S4	S5	S6	S7
S1	0.841							
S2	1.048	28.834						
S3	0.948	3.348	39.413					
S4	0.961	1.579	6.741	61.411				
S5	1.095	8.925						
S6	1.275		8.925			28.834		
S7	1.063			8.925		3.348	39.413	
Ex	1.069				8.925	1.579	6.741	61.411

I3-1	GS	S1	S2	S3	S4	S5	S6	S7
S1	1.831							
S2	0.587	14.513						
S3	0.754	1.293	26.92					
S4	1.157	1.41	4.818	41.528				
S5	1.186	4.926						
S6	0.593		4.926			14.513		
S7	0.723			4.926		1.293	26.920	
Ex	0.946				4.926	1.41	4.818	41.528

F-doping

T1-1	GS	S1	S2	S3	S4	S5
S1	0.732					
S2	1.611	25.300				
S3	2.310	6.329	44.82			
S4	0.642	0.619	x	x		
S5	0.949	x	0.619	x	25.300	
Ex	1.049	x	x	0.619	6.329	44.82

E2-6	GS	S1	S2	S3	S4	S5
S1	2.444					
S2	0.968	25.132				
S3	1.764	5.591	45.177			
S4	0.482	4.172				
S5	0.707		4.172		25.132	
Ex	0.978			4.172	5.591	45.177

F2-1	GS	S1	S2	S3	S4	S5
S1	0.275					
S2	0.828	20.891				
S3	1.102	4.556	32.409			
S4	0.292	2.049				
S5	0.593		2.049		20.891	
Ex	0.735			2.049	4.556	32.409

F3-9	GS	S1	S2	S3	S4	S5
S1	1.426					
S2	0.898	25.782				
S3	1.587	4.891	53.038			
S4	0.380	3.381				
S5	0.447		3.381		25.782	
Ex	0.675			3.381	4.891	53.038

I3-1	GS	S1	S2	S3	S4	S5
S1	0.523					
S2	1.358	20.253				
S3	1.916	3.229	41.598			
S4	0.389	2.249				
S5	0.665		2.249		20.253	
Ex	0.87			2.249	3.229	41.598

Table S5. Comparison of radiative and non-radiative electron-hole recombination time.

	N-doped TiO_2		F-doped TiO_2	
	Radiative (μs)	Non-radiative (ps)	Radiative (μs)	Non-radiative (ps)
Pristine	2.013	873.553	2.013	118.789
T1-1	4.895	320.136	2.208	245.726
E2-6	1.199	512.264	7.348	18.784
F2-1/F2-3	0.916	1057.807	5.146	1483.210
F3-9	1.009	1016.100	11.831	213.088
I3-1	1.484	873.553	6.613	807.044