SUPPLEMENTAL INFORMATION

Charge Transfer, Luminescence, and Phonon Bottleneck in TiO_2 Nanowires Computed by Eigenvectors of Liouville Super-operator

Shuping Huang and Dmitri S. Kilin*

Department of Chemistry, University of South Dakota, Vermillion, USA

*Corresponding author. Email: Dmitri.Kilin@usd.edu

Table S1 The eigen-frequencies for different eigen-states of electron and hole.

ν	Ω_ν^e, ps^{-1}	Ω_ν^h, ps^{-1}	ν	Ω_ν^e, ps^{-1}	Ω_ν^h, ps^{-1}
1	0	0	16	-23.4271	-9.0417
2	-0.1741	-0.8784	17	-20.2322	-12.4454
3	-14.9446	-6.7749	18	-12.1781	-9.3268
4	-6.2908	-8.0324	19	-12.5798	-9.6351
5	-4.7513	-8.3321	20	-22.0363	-10.5402
6	-23.1321	-11.6736	21	-33.0708	-18.6037
7	-17.5023	-10.3328	22	-29.7486	-6.4002
8	-13.6718	-11.8456	23	-12.674	-19.0821
9	-9.1904	-7.0828	24	-13.0171	-22.5147
10	-10.2745	-17.2176	25	-19.193	-4.6065
11	-16.9477	-22.5849	26	-9.7449	-10.6745
12	-12.2228	-12.0594	27	-16.0566	-27.1332
13	-13.9338	-7.8697	28	-30.1739	-16.6317
14	-16.0326	-3.806	29	-14.6955	-21.2329
15	-32.5292	-4.7232	30	-19.3557	-9.9668

Table S2. Electron and hole energy dissipation rates K_e and K_h of featured electronic transitions of bulk TiO_2.

Transition energy (eV)	Oscillator Strength	Hole index (*iH*)	Electron Index (*iE*)	K_e, ps^{-1}	K_h, ps^{-1}	K_e+K_h, ps^{-1}
2.2829	5.7912	8	1	0.0	0.1712	0.1712
2.2829	5.7912	7	1	0.0	0.1485	0.1485
2.2860	3.1631	5	3	0.2066	6.9634	7.1700
2.2860	3.1630	6	2	0.0975	4.7892	4.8867
2.2860	3.0607	6	3	0.2066	4.7892	4.9958
2.2860	3.0606	5	2	0.0975	6.9634	7.0609
3.0231	1.7424	3	6	0.0974	11.5972	11.6946
3.0231	1.7424	4	5	0.0888	10.4945	10.5833
3.0230	1.7424	2	7	0.1834	13.7709	13.9543
3.0230	1.7424	1	8	0.1927	0.0	0.1927

Table S3. Electron and hole energy dissipation rates K_e and K_h of featured electronic transitions of anatase (101) TiO_2 surface.

Transition energy (eV)	Oscillator Strength	Hole index (*iH*)	Electron Index (*iE*)	K_e, ps^{-1}	K_h, ps^{-1}	K_e+K_h, ps^{-1}
2.1235	1.5070	5	2	3.8320	2.4469	6.2789
2.6691	1.4997	8	11	2.5947	2.6578	5.2525
2.8308	1.1155	25	9	2.6202	2.9183	5.5385
2.3137	1.0822	17	1	0.0	2.7042	2.7042
2.5645	1.0740	8	10	2.6293	2.6578	5.2871
2.6778	1.0205	17	9	2.6202	2.7042	5.3244
2.2320	0.9631	13	1	0.0	2.5654	2.5654

The analytic solutions of Eqs. 13(a)-(c).

Eq. 13(c) is easy to be solved, and then its solution is substituted into Eq. 13(b). The ordinary differential equation Eq. 13(b) is solved by Laplace method. Finally the solution of Eq. 13(b) and 13(c) is substituted into Eq.13(a), and Eq. 13(a) can be solved.

The analytic solutions of 13(a), 13(b) and 13(c) are as follows:

$$\rho_{LU,LU} = 1 - \frac{R_{LU,LU+1}R_{LU+1,LU+2}+R_{LU,LU+1}R_{LU,LU+2}-R_{LU+1,LU+2}R_{LU,LU+2}-R_{LU,LU+2}^2}{(R_{LU,LU+2}+R_{LU+1,LU+2})(R_{LU,LU+1}-R_{LU+1,LU+2}-R_{LU,LU+2})} e^{-(R_{LU,LU+2}+R_{LU+1,LU+2})t} + \frac{R_{LU+1,LU+2}}{R_{LU,LU+1}-R_{LU+1,LU+2}-R_{LU,LU+2}} e^{-R_{LU,LU+1}t} \quad \text{(S1a)}$$

$$\rho_{LU+1,LU+1} = \frac{R_{LU+1,LU+2}}{R_{LU,LU+1}-R_{LU+1,LU+2}-R_{LU,LU+2}} [e^{-(R_{LU+1,LU+2}+R_{LU,LU+2})t} - e^{-R_{LU,LU+1}t}] \quad \text{(S1b)}$$

$$\rho_{LU+2,LU+2} = e^{-(R_{LU+1,LU+2}+R_{LU,LU+2})t} \quad \text{(S1c)}$$

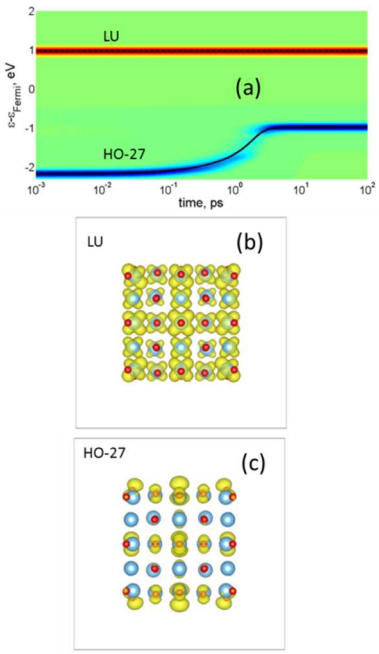

Figure S1 (a) Non-adiabatic relaxation dynamics of the strongest optical transition (with the largest oscillator strength) for <001> NW. Here, red, green, and blue coloured areas label the distribution $\Delta n^{(a,b)}(\varepsilon,t)$ in Eq. 7 for gain, no change, and loss, respectively, in comparison with the equilibrium distribution; red areas can be understood as relating to electrons, and blue ones to holes. (b) - (c) The top views of partial charge densities for HO-27 and LU orbitals at Γ point. Ti atoms are in blue, and O atoms are in red.