*Supporting information for*

# Unraveling the Quantum Dynamics Origin of High Photocatalytic Activity in Nitrogen Doped Anatase $TiO_2$: Time-Domain Ab Initio Study

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**S1. State-to-state transition rate and the coupled kinetics equations.**

**Figure S1** shows the time evolution population of the first excited state (conduction band minimum, CBM) and trap states for the transition of pairs of electronic states in the pristine $TiO_2$, N(0) and N(-1) systems. Fitting the curves to an exponent: $P(t) = exp^{[0]}(-\frac{t}{\tau})$, gives the relaxation time, $\tau$. The inverse value of $\tau$ corresponds to the state-to-state transition rates $k_{(cbm\rightarrow vbm)}$, $k_{(cbm\rightarrow etrap)}$, $k_{(etrap\rightarrow vbm)}$ and $k_{(vbm\rightarrow htrap)}$ for the pairs of electronic states, which are labelled in **Figure S1**, **Tables 1** and **S1**. By solving the coupled kinetic equations with the obtained rate constants, we obtained the charge trapping and recombination dynamics, Figure 7 in main text. **Figures S2-S3** give the basis set. The $[ES]$, $[GS]$ and $[trap]$ correspond to the CBM, valence band maximum (VBM) and the electron or hole trap states.

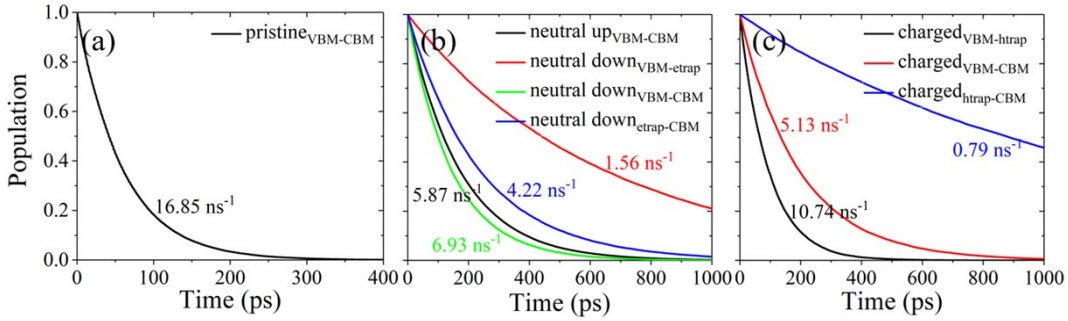


**Figure S1.** Time evolution of the considered pair population of **(a)** pristine anatase $TiO_2$, **(b)** neutral N-doped $TiO_2$, and **(c)** negatively charged N-doped $TiO_2$. Black, red, green and blue curves in **Figure S1(b)** stand for population of VBM-CBM (spin-up), VBM-etrap state (spin-down), VBM-CBM (spin-down) and etrap state-CBM (spin-down) in neutral N-doped $TiO_2$. It is similar in **Figure S1(c)**. The calculated rate constants are summarized in **Table 1** and **Table S1**.

**(1) N(0) system:** electron trap-assisted electron-hole recombination process.

$$\frac{d[ES]}{dt} = -(k_{cbm\rightarrow etrap} + k_{cbm\rightarrow vbm})[ES]$$

$$\frac{d[trap]}{dt} = k_{cbm\rightarrow etrap}[ES] - k_{etrap\rightarrow vbm}[trap]$$

$$\frac{d[GS]}{dt} = k_{cbm\rightarrow vbm}[ES] + k_{etrap\rightarrow vbm}[trap]$$

The solutions of above equations:

$$[ES] = e^{-(k_{cbm\rightarrow etrap} + k_{cbm\rightarrow vbm}) * t}$$

$$[trap] = \frac{k_{cbm\rightarrow etrap}}{k_{cbm\rightarrow etrap} + k_{cbm\rightarrow vbm} - k_{etrap\rightarrow vbm}}[e^{-k_{etrap\rightarrow vbm} * t} - e^{-(k_{cbm\rightarrow etrap} + k_{cbm\rightarrow vbm}) * t}]$$

$$[GS] = 1 - [ES] - [trap]$$

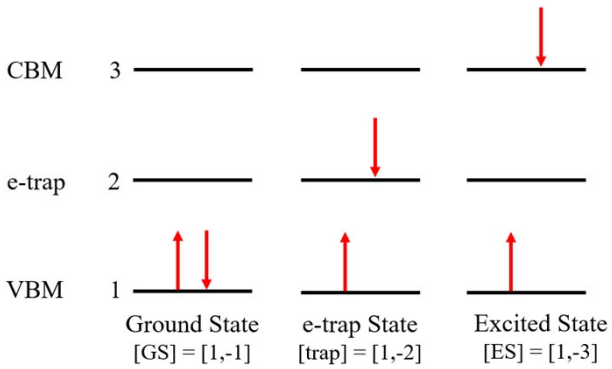


**Figure S2.** Schematic diagram for electron trap-assisted electron-hole recombination in the N(0) system.

**(2) N(-1) system:** hole trap-assisted electron-hole recombination process,

$$\frac{d[ES]}{dt} = -(k_{htrap\rightarrow vbm} + k_{cbm\rightarrow vbm})[ES]$$

$$\frac{d[trap]}{dt} = k_{htrap\rightarrow vbm}[ES] - k_{cbm\rightarrow htrap}[trap]$$

$$\frac{d[GS]}{dt} = k_{cbm\rightarrow vbm}[ES] + k_{cbm\rightarrow htrap}[trap]$$

The solutions of above equations:

$$[ES] = e^{-(k_{htrap\rightarrow vbm} + k_{cbm\rightarrow vbm}) * t}$$

$$[trap] = \frac{k_{htrap\rightarrow vbm}}{k_{htrap\rightarrow vbm} + k_{cbm\rightarrow vbm} - k_{cbm\rightarrow htrap}}[e^{-k_{cbm\rightarrow htrap} * t} - e^{-(k_{htrap\rightarrow vbm} + k_{cbm\rightarrow vbm}) * t}]$$

$$[GS] = 1 - [ES] - [trap]$$

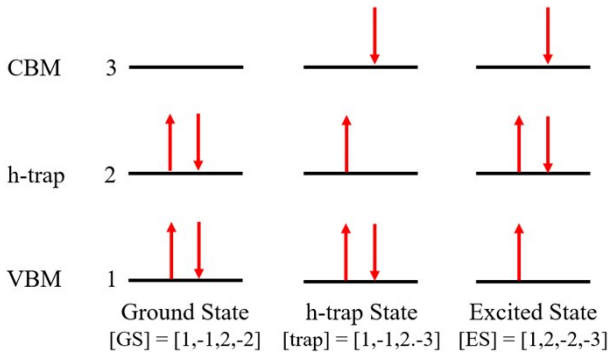


**Figure S3.** Schematic diagram for hole trap-assisted electron-hole recombination in the N(-1) system.

**S2. Charge density of spin-up channel for pristine anatase $TiO_2$, $TiO_2$ doping with neutral and negatively charged N.**

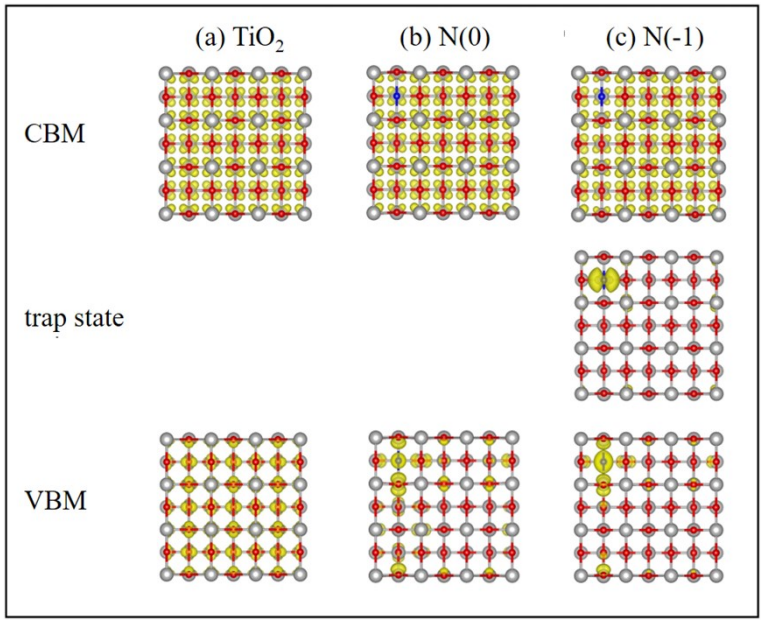


**Figure S4.** Spin-up charge densities of VBM, trap-state and CBM for (**a**) anatase $TiO_2$, (**b**) N(0) and (**c**) N(-1). The charge densities of pristine and N(-1) systems remain unchanged to those in the spin-down channel shown in Figure 4 in the main text. The cancellation of electron trap state in the spin-up channel of N(0) system delays electron-hole recombination compared to that in the spin-down channel.

**S3. Characteristics in neutral N-doped $TiO_2$ in the spin-up channel.**

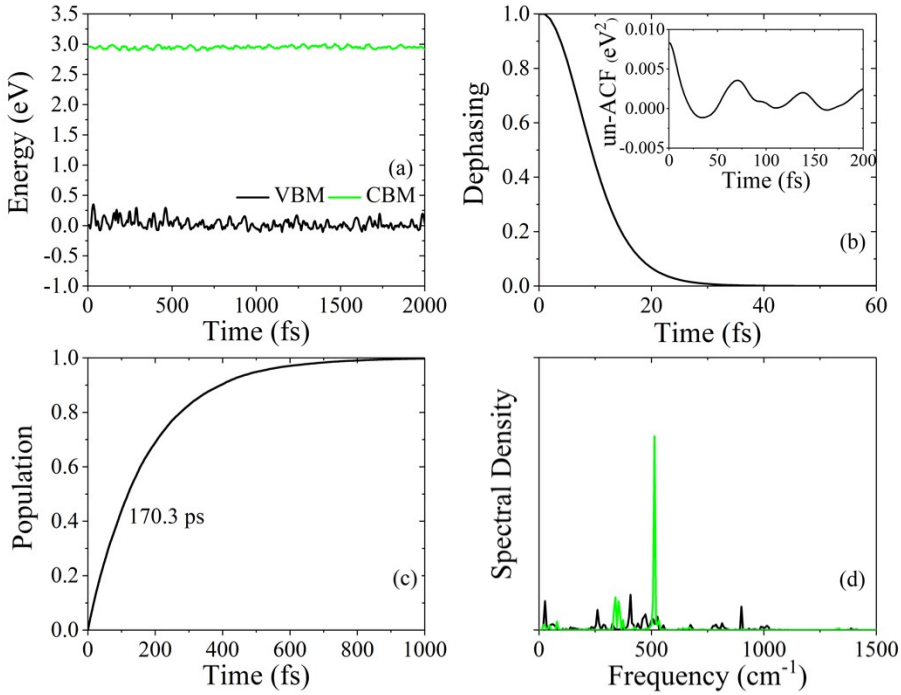


**Figure S5. (a)** Time evolution of the VBM and CBM energies, **(b)** Pure-dephasing functions and inset of unnormalized ACF, **(c)** electron-hole recombination dynamics and **(d)** spectral density of the VBM and CBM for neutral N-doped $TiO_2$ in the spin-up channel.

**Table S1**. Bandgaps, average absolute non-adiabatic coupling (NAC), pure-dephasing time, and quantum transition rate constant for CBM-VBM transition of neutral N-doped anatase $TiO_2$ in the spin-up channel.

| | **Bandgap (eV)** | **NAC (meV)** | **Dephasing (fs)** | **Rate ($ns^{-1}$)** |
|---|---|---|---|---|
| $\mathbf{N(0)}_{\mathbf{CBM \rightarrow VBM}}$ | 2.92 | 1.79 | 8.1 | 5.87 |