Supporting Information

A hybrid density functional theory study of the anion distribution and applied electronic properties of the LaTiO₂N semiconductor photocatalyst

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Section 1. The temperature well



Figure S1 the diagram of the pyrolysis temperature/energy-well, E_P stands for the corresponding enthalpy for the pyrolysis temperature.

Figure S1 gives the diagram of the temperature well. There is a simplified relationship between enthalpy change and temperature on the condition of high temperature ($h\sigma / k_B T \ll 1$) condition¹⁸:

$$\Delta E|_{T} \approx \left(\frac{\partial \overline{U}}{\partial T}\right)_{V} T + V \Delta P \approx k_{B} T + V \Delta P$$
(S1)

where k_B is Boltzmann constant, U is internal energy and P/V is pressure/volume. The open heating system for a solid suggests the heating-process is not quasistatic but level pressure-volume nonequilibrium thermal process, therefore, the V ΔP is zero and the entropy generation is positive, the enthalpy change then is underestimated based on the definition Equation S1. Considering the two models in Figure S1, if the energy of M_{struct} gets beyond of the pyrolysis energy barrier E_P (equal to $k_B T_P$), the M_{struct} will be conditional stability while the Equation S1 narrows the allowed energy range, therefore, the criterion above should be strict in the judge of relative stability but not relative instability. Besides, the primitive cell M_{struct} should be stable and could not transform into M_{stable} because of the energy barrier between electronic orbits and nearly-free electronic energies. Evidence here is that, if the transform could proceed spontaneously, the junction energy between M_{struct} and M_{stable} will have a higher energy than the M_{stable}, unfortunately, this is opposite to the calculated result for the typical junctions of LaTiO₂N in Figure S4. Generally, if the M_{struct} is thermal stable, a sufficient condition is that the structure being within the energy barrier $\Delta E \approx k_B T_P$ to the M_{stable}, corresponding to the temperature barrier between the pyrolysis Temperature (i.e. T_P in Figure S6) and absolute zero.

Section 2. The anion Site of the 27 possible primitive cell structures.

The detailed atomic structures of the 27 possible LaTiO₂N primitive cell structures can be found in Table. S1. The N and O atoms in each Site are listed as the $n_{o,j}^k / n_{N,j}^k$ in the table. The positions of the three sites are shown in Fig. S2.



Figure S2. The three-anion sites in $LaTiO_2N$ primitive cell: the three anion sites, Site-1, Site-2

and Site-3, located at the vertexes of the Ti-anion octahedron.

Table S1. The O/N anions occupation at the three Sites in a primitive cell for

Structure/M _k	The number of N and O atoms in LaTiO ₂ N structures($n_{o,j}^k / n_{N,j}^k$)							
	Primeval cell(total)		Site-1		Site-2		Site-3	
	N	0	Ν	0	Ν	0	N	0
M ₁	2	4	1	1	1	1	0	2
M_2	2	4	0	2	1	1	1	1
M ₃	2	4	1	1	0	2	1	1
M_4	2	4	2	0	0	2	0	2
M ₅	2	4	0	2	2	0	0	2
M_6	2	4	0	2	0	2	2	0
M_7	1	5	1	1	0	2	0	2
M_8	1	5	0	2	1	1	0	2
M ₉	1	5	0	2	0	2	1	1
M_{10}	0	6	0	2	0	2	0	2
M ₁₁	3	3	1	1	1	1	1	1
M ₁₂	3	3	2	0	1	1	0	2
M ₁₃	3	3	2	0	0	2	1	1
M ₁₄	3	3	1	1	2	0	0	2
M ₁₅	3	3	0	2	2	0	1	1
M ₁₆	3	3	1	1	0	2	2	0
M ₁₇	3	3	0	2	1	1	2	0
M ₁₈	4	2	0	2	2	0	2	0
M ₁₉	4	2	2	0	0	2	2	0
M ₂₀	4	2	2	0	2	0	0	2
M ₂₁	4	2	1	1	1	1	2	0
M ₂₂	4	2	1	1	2	0	1	1
M ₂₃	4	2	2	0	1	1	1	1
M ₂₄	5	1	1	1	2	0	2	0
M ₂₅	5	1	2	0	1	1	2	0
M ₂₆	5	1	2	0	2	0	1	1
M ₂₇	6	0	2	0	2	0	2	0

structures M1~M27.

Section 3. The divacancies for the M₁~M₃

The divacancies of typical primitive cell structures $M_1 \sim M_3$, the vacancy energies of divacancies are higher than that of mo novacancies.



Figure S3 the divacancies for the M₁~M₃ primitive cell structures

Section 4. The acceptable primitive cell structure contents and corresponding vacancy rates for anion ratio condition calculation

The solutions $\{X_k|_{k=1,2,3,8,9}\}$ for the anion ratio equations are obtained as the functions of the vacancy rates $f(\phi_{13}, \phi_{21}, \phi_{22}, \phi_{23}, \phi_{32})$. Here N vacancy matrix obtains zero and O vacancy matrix are:

$$\left. \phi_{kj} \right|_{k=1,2,3,8,9} = \begin{bmatrix} 0 & 0 & \phi_{13} & 0 & 0 \\ \phi_{21} & \phi_{22} & \phi_{23} & 0 & 0 \\ 0 & \phi_{22} & 0 & 0 & 0 \end{bmatrix}$$
(S2)

The numerical solutions of primitive cell contents by discrete method are presented in Fig. S4(a). As can be seen, the percentage of M_1 is exactly lower than 5%, having a great gap of more than 15% to the four left structures. In addition, Figure S4(b) gives

the Gauss-fitting curve about the percentage of M_1 with the total oxide fraction, as can be seen, the percentage of M_1 is asymptotic with respect to the zero point with the oxide fraction rise; it means that the percentage of M_1 drops rapidly to zero on the condition of oxygen rich. As known the LaTiO₂N crystal is oxygen rich, accordingly M_1 should be out of LaTiO₂N.



Figure S4(a).The ligature curve for the percentage of $M_{1,2,3,8,9}$ in LaTiO₂N with the rise of total vacancy rate. (b). the ligature and Gauss fitting curve for the percentage of M_1 in LaTiO₂N with the rise of total oxide fraction.

Figure S5 shows the scatter and Gauss-fitting curve of the vacancy rate with the total oxide fraction rise. As can be seen, the vacancy rates ϕ_{21} and ϕ_{22} (stands for the vacancy rate for M₂ at Site-1 and Site-2), are exactly equal to zeroes with the oxide fraction rise. It means that the two types of vacancy should be out of LaTiO₂N on the condition of oxygen rich. In addition, the vacancy rates ϕ_{23} and ϕ_{32} are positive and the vacancy structures M₂/Site-3 and M₃/Site-2 should be found in LaTiO₂N, respectively.



Figure S5. The scatter and corresponding Gauss fitting curve of the vacancy rate for M₂/Site-1,
2, 3 and M₃/Site-2 in a LaTiO₂N, with the rise of total oxide fraction.

In general, the proposal acceptable primitive cell group of $LaTiO_2N$ contains four non-vacancy structures $M_{2,3,8,9}$ and two anion vacancy structures M_2/M_3 at Site-3/2.

Section 5. The junction between the acceptable primitive cell structures.

Figure S6 shows the junction between the acceptable primitive cell structures, as can be seen, the junction binding energies (i.e. the dark points) are much higher than pure structures of the lowest one (i.e. M_2/M_3 in the red points), indicating that the primitive cells of each structures will achieve self-aggregation instead of mixed lattice with other structure cells.



Figure S6. The binding energy of homojunction between acceptable primitive cell structures.