

Supplementary Information

Band-tail states mediated visible-light-driven water splitting in $\text{Y}_2\text{Ti}_2\text{O}_5\text{S}_2$ photocatalyst

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Methods

1. Asymmetric double sigmoidal (Asym2Sig) model for PL fitting. PL spectrum measured in Fig. 2a was fitted using asymmetric double sigmoidal (Asym2Sig) model¹:

$$y = y_0 + A \times \frac{1}{1 + e^{-\frac{x - x_c + \frac{W_1}{2}}{W_2}}} \times \left(1 - \frac{1}{1 + e^{-\frac{x - x_c - \frac{W_1}{2}}{W_3}}} \right) \quad (\text{S1})$$

where y_0 and A are constants, x_c is the peak energy, W_1 is the full width at half maximum, W_2 is variance of low-energy side, and W_3 is variance of high-energy side.

2. Calculation of defect formation energy. Defect formation energy ΔH in the process of forming compound AB from element A and B is expressed as: $E(A) + E(B) + \Delta H = E(AB)$. When studying a defect system, a system (host) without defects should be chosen as a reference first. For a defect α with charge q , its formation energy $\Delta H^f(\alpha, q)$ can be rewritten as²:

$$\Delta H^f(\alpha, q) = E(\alpha, q) - E(\text{host}) - \sum_i n_i (E_i + \mu_i) + q(E_f + E_{VBM}(\text{host}) + \Delta V) \quad (\text{S2})$$

where $E(\alpha, q)$ is the total energy of the defect system, $E(\text{host})$ is the total energy of the reference system, E_{VBM} is the VBM energy of reference system, E_f is the Fermi level referenced to the VBM of the host, E_i is the energy of the corresponding simple substance, and μ_i is the chemical potential of the element. ΔV is the correction term to align the reference potential in our defect supercell with that in the bulk. According to Eq. (S2), in order to calculate the formation energy of intrinsic point defects in $Y_2Ti_2O_5S_2$, the chemical potential range of each constituent element should be determined first.

The chemical potential is thermodynamically limited by a series of conditions:

(i) the sum of the chemical potentials of each component element must be in equilibrium with the compound formation energy, that is, it must satisfy the equation:

$$2\mu_Y + 2\mu_{Ti} + 2\mu_S + 5\mu_O = \Delta H_f^{Y_2Ti_2O_5S_2} \quad (\text{S3})$$

(ii) $\mu_S=0$ means that sulfur is abundant enough to form elemental sulfur, but it should need to avoid this situation, which requires the chemical potential of the four elements to be less than 0 ($\mu_S < 0$, $\mu_O < 0$, $\mu_Y < 0$, and $\mu_{Ti} < 0$).

(iii) to avoid the formation of secondary phases, the chemical potential also needs to satisfy the following inequalities:

$$2\mu_Y + 3\mu_O < \Delta H_f^{Y_2O_3} \quad (S4)$$

$$\mu_{Ti} + 2\mu_O < \Delta H_f^{TiO_2} \quad (S5)$$

$$\mu_{Ti} + 2\mu_S < \Delta H_f^{TiS_2} \quad (S6)$$

$$2\mu_Y + 2\mu_S + \mu_O < \Delta H_f^{Y_2O_3O} \quad (S7)$$

Under these established constraints, the chemical potential ranges of Y, Ti, and S that stabilize the $Y_2Ti_2O_5S_2$ compound are incorporated in a polyhedron of three-dimensional (μ_Y, μ_{Ti}, μ_S) space.

References

1. J. Krustok, H. Collan, M. Yakushev and K. Hjelt, *Phys. Scripta.*, 1999, **1999**, 179.
2. S. Chen, J.-H. Yang, X. G. Gong, A. Walsh and S.-H. Wei, *Phys. Rev. B*, 2010, **81**, 245204.

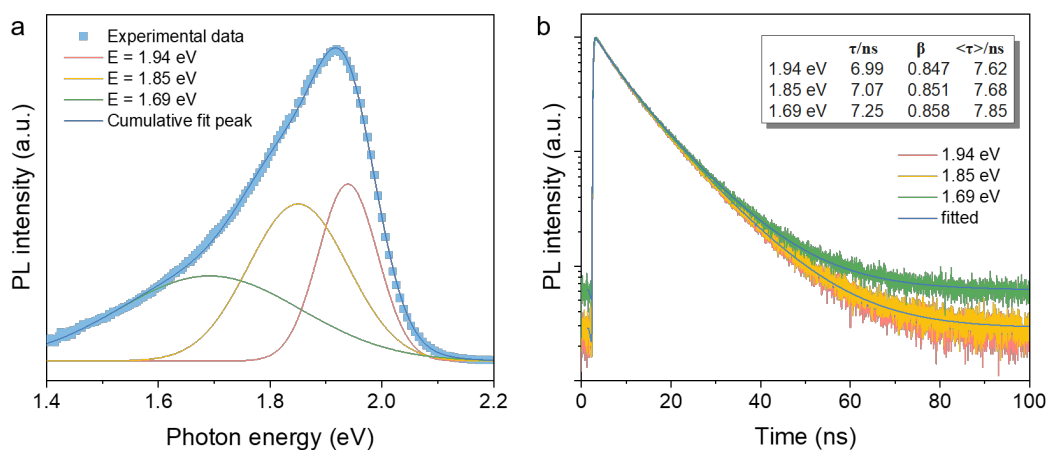


Fig. S1 Room-temperature PL spectra of the $\text{Y}_2\text{Ti}_2\text{O}_5\text{S}_2$ powder. (a) Room-temperature PL spectrum of $\text{Y}_2\text{Ti}_2\text{O}_5\text{S}_2$ powder measured under 510 nm laser excitation. The spectrum can be well fitted by three Gaussian bands with peaks at 1.69 eV, 1.85 eV and 1.94 eV. (b) Room temperature TRPL spectra measured at 1.69 eV, 1.85 eV and 1.94 eV. Inset shows the fitting results using stretched exponential decay.

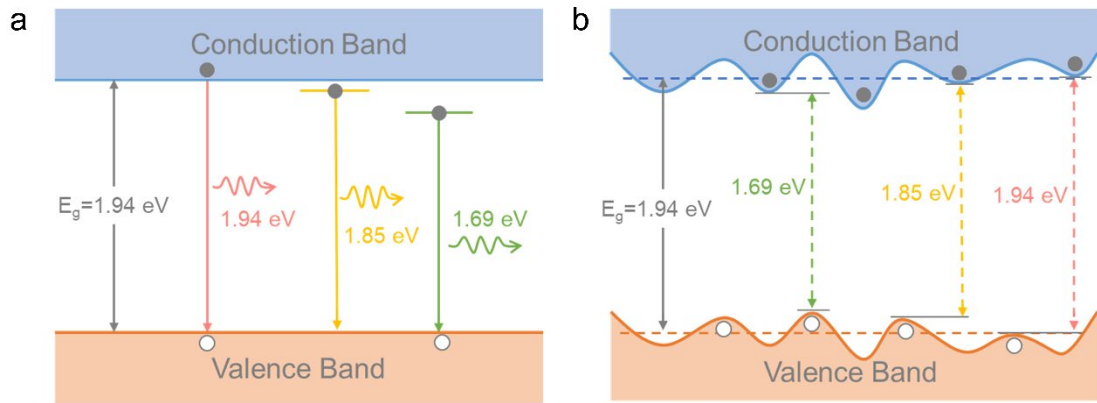


Fig. S2 Schematic diagrams of PL mechanism corresponding to different room-temperature emission mechanisms in $\text{Y}_2\text{Ti}_2\text{O}_5\text{S}_2$. (a) Some of the possible PL processes in $\text{Y}_2\text{Ti}_2\text{O}_5\text{S}_2$. The 1.94 eV emission is attributed to recombination of conduction electrons with valence holes. The 1.85 eV and 1.69 eV emissions are attributed to recombination between conduction electrons and excited holes through defect levels. (b) Schematic drawing of the mechanism of band-tail state recombination. The grey and white circles represent electrons and holes, respectively.

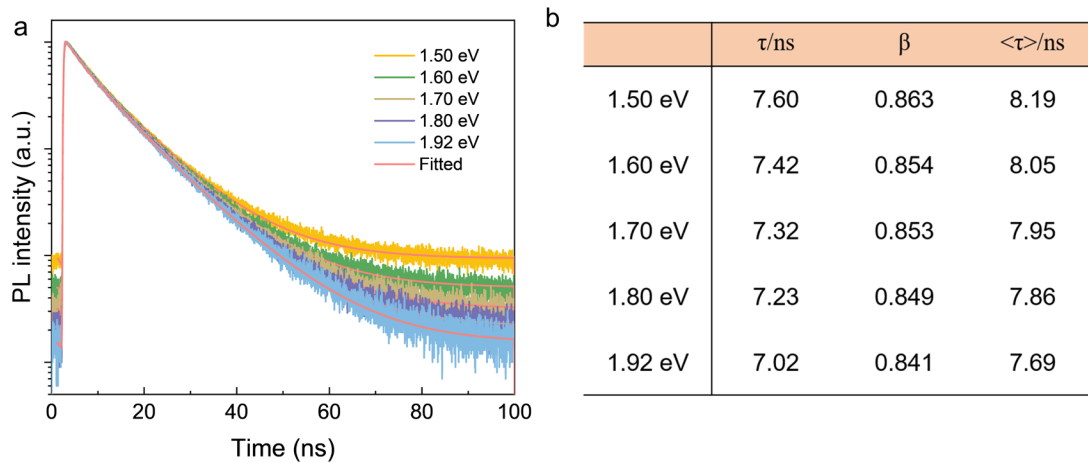


Fig. S3 Room-temperature TRPL spectra of the $\text{Y}_2\text{Ti}_2\text{O}_5\text{S}_2$ powder measured at different position. (a) Room-temperature TRPL spectrum measured under 510 nm laser excitation. (b) The fitted parameters for the TRPL decay at different position using stretched exponential decay.

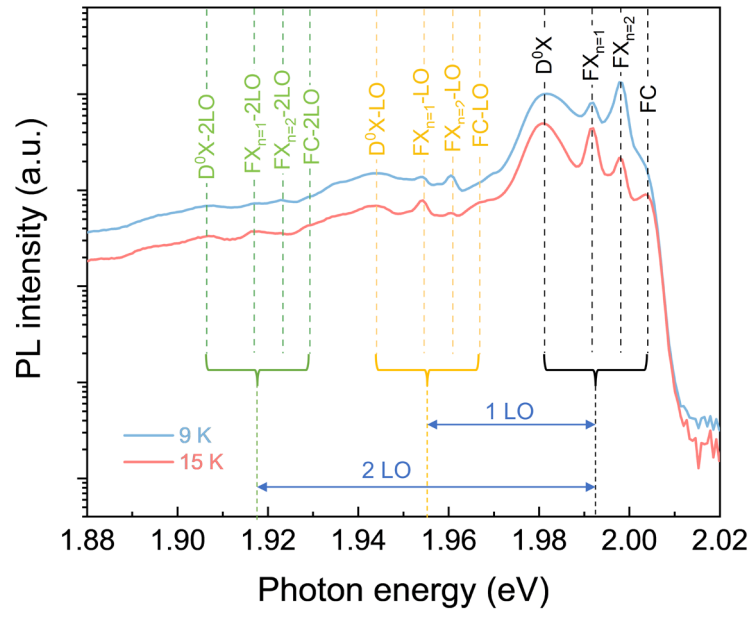


Fig. S4 Low-temperature PL spectra of $\text{Y}_2\text{Ti}_2\text{O}_5\text{S}_2$ powder. The PL spectra were measured under 420 nm laser excitation at 9 and 15 K.

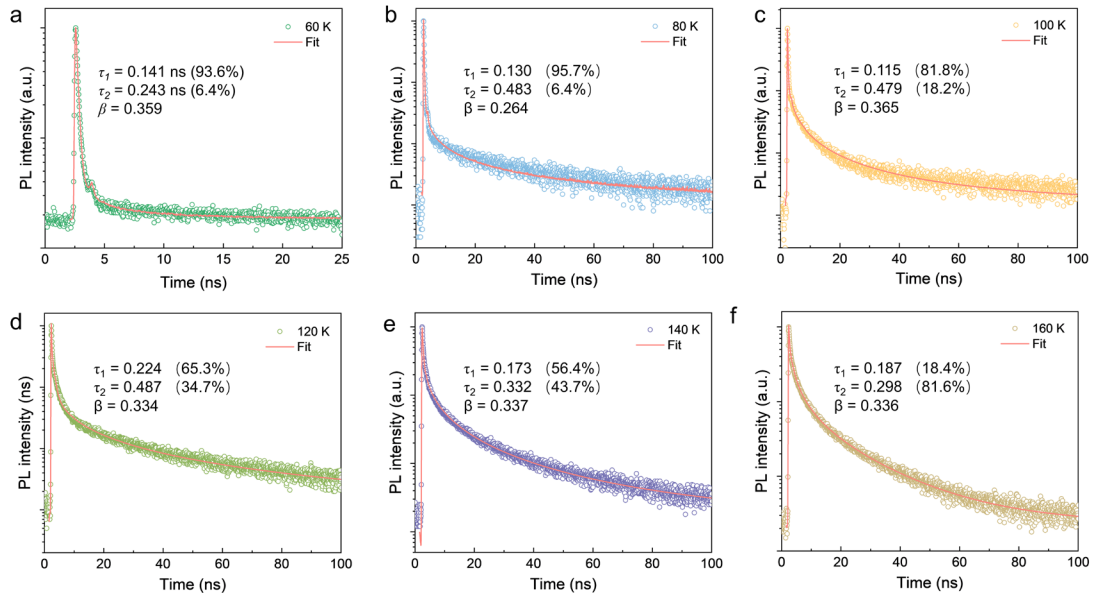


Fig. S5 TRPL decay curves of $\text{Y}_2\text{Ti}_2\text{O}_5\text{S}_2$ measured at different temperatures between 60-160 K. (a) 60 K. (b) 80 K. (c) 100 K. (d) 120 K. (e) 140 K. (f) 160 K. Circles indicate experimental data, and the red line shows the fitted curve using thermalized stretching exponential decay. The detailed fitting parameters are listed in Table S2.

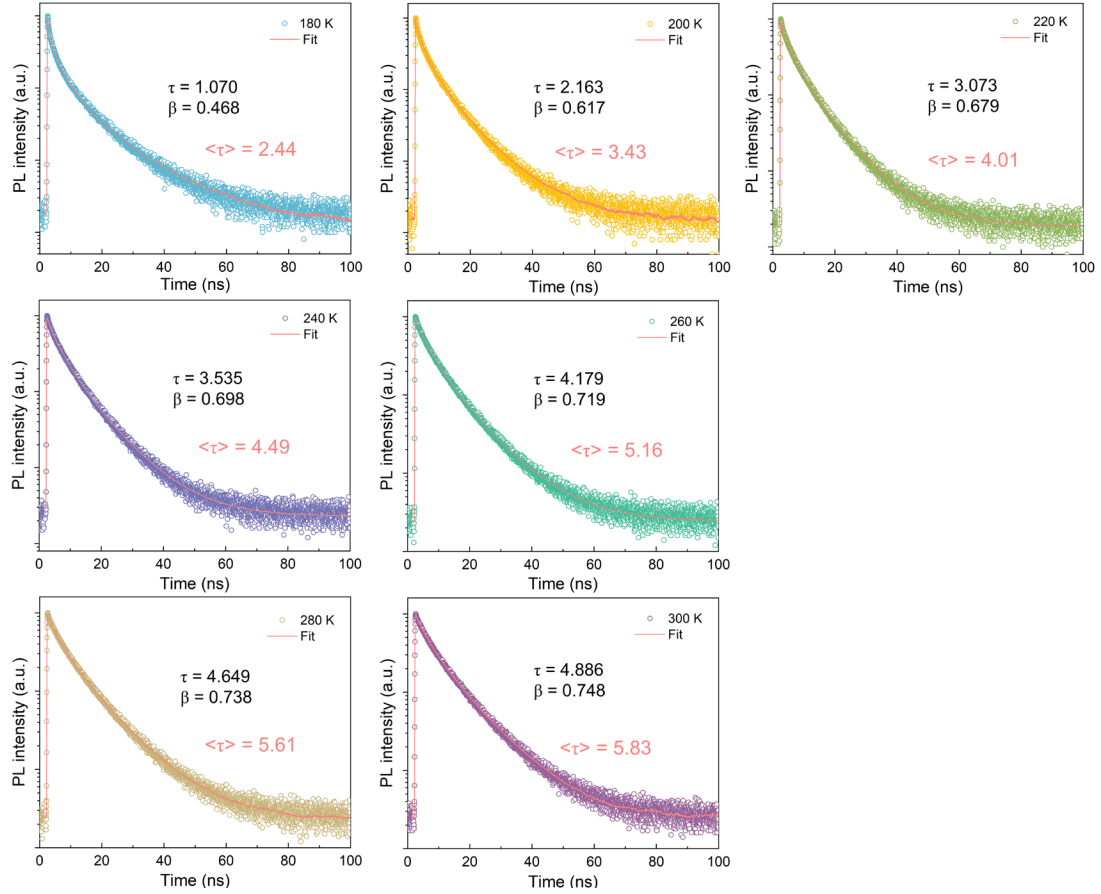


Fig. S6 TRPL decay curves of $\text{Y}_2\text{Ti}_2\text{O}_5\text{S}_2$ measured at different temperatures between 180-300 K. (a) 180 K. (b) 200 K. (c) 220 K. (d) 240 K. (e) 260 K. (f) 280 K. (g) 300 K. Circles indicate experimental data, and the red line shows the fitted curve using stretched exponential decay. The detailed fitting parameters are listed in Table S3.

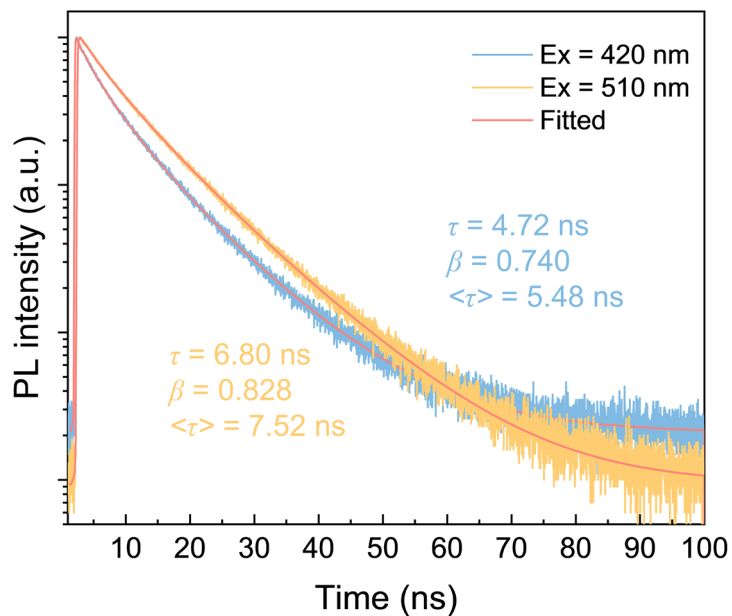


Fig. S7 TRPL decay curves of $\text{Y}_2\text{Ti}_2\text{O}_5\text{S}_2$ measured under different excitation lasers. The curves were measured at room temperature in air under 420 and 510 nm laser excitation. The red line shows the fitting of the decay with a stretched exponential decay (Eq. (1)). Inset shows the fitted parameters of the stretched exponential decay.

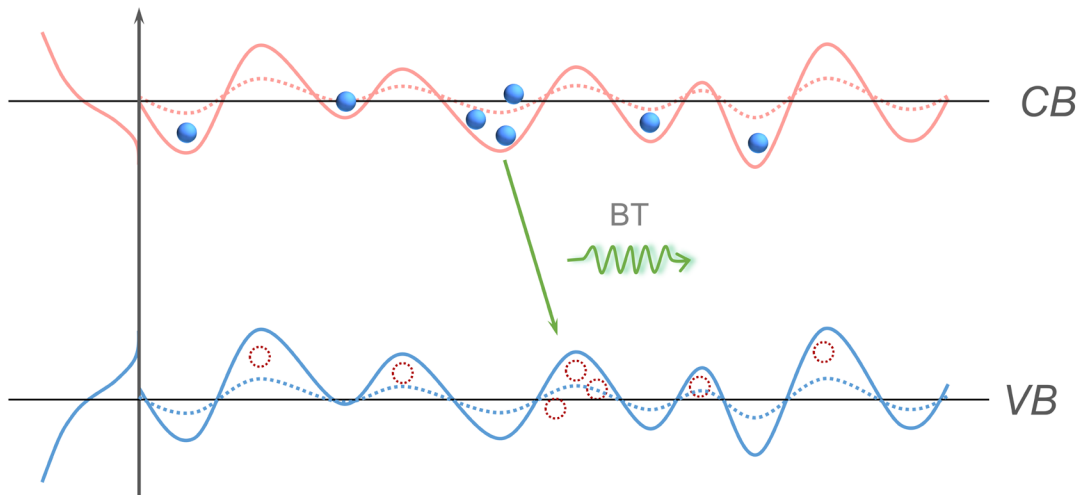


Fig. S8 Schematic diagrams of the mechanism of band-tail recombination in $Y_2Ti_2O_5S_2$. The amplitude of the spatial potential fluctuation increases with increasing temperature. The dashed line represents the band structure at low temperature, while the solid line represents the band structure at high temperature.

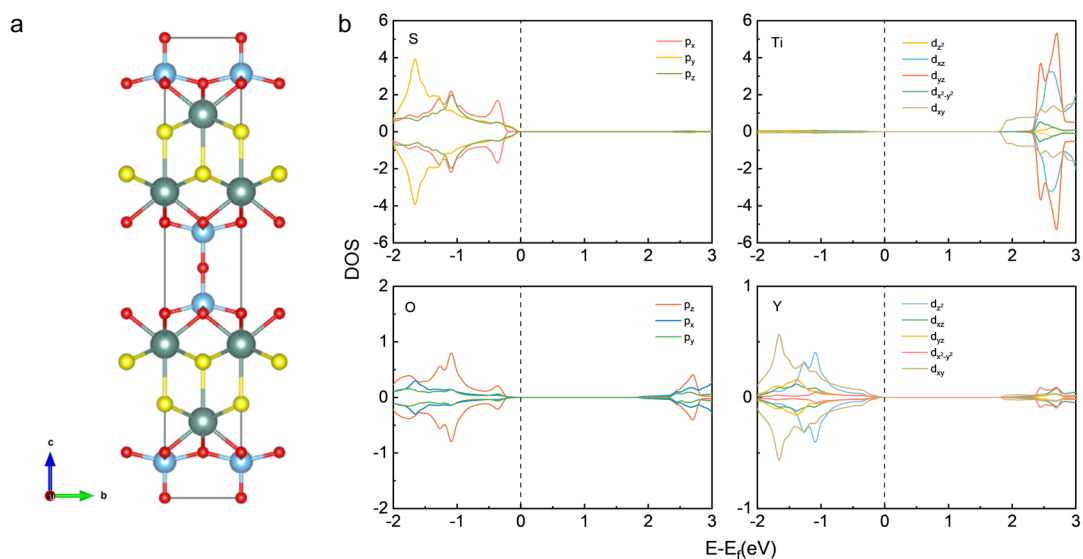


Fig. S9 DFT calculations of $\text{Y}_2\text{Ti}_2\text{O}_5\text{S}_2$ photocatalyst. (a) Atomic structure of $\text{Y}_2\text{Ti}_2\text{O}_5\text{S}_2$. The red, blue, green, and yellow balls represent O, Ti, Y, and S atoms, respectively. $\text{Y}_2\text{Ti}_2\text{O}_5\text{S}_2$ is a layered oxysulfide consisting of an alternating stacking of Ti_2O_5 double layer unit and Y_2S_2 layer unit with the space group of $I4/mmm$. Our PBE+U calculated lattice constants: $a = b = 3.847 \text{ \AA}$ and $c = 23.168 \text{ \AA}$. (b) Partial density of states of S-3p, Ti-3d, O-2p, and Y-4d orbitals. The Fermi level is set to zero.

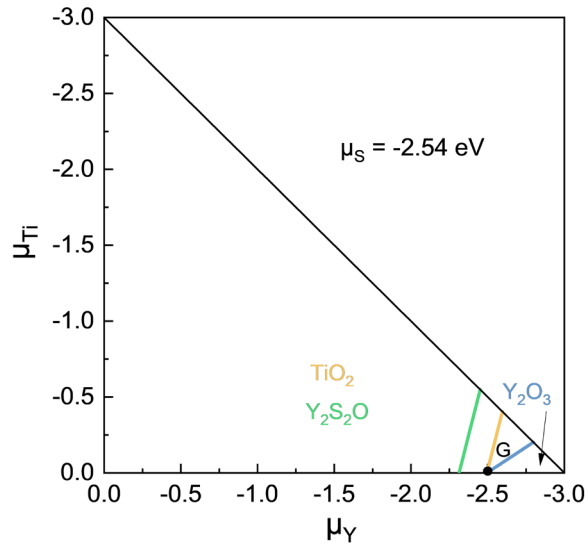


Fig. S10 The calculated stable chemical-potential region in the $\mu_S = -2.54 \text{ eV}$ plane. The stable region on the $\mu_S = -2.54 \text{ eV}$ section consists only one point (G point), and a slight deviation of the chemical potential on this plane produces a secondary phase of Y_2O_3 , TiO_2 , which indicates that G is one of the end points of a three-dimensional stable polyhedron.

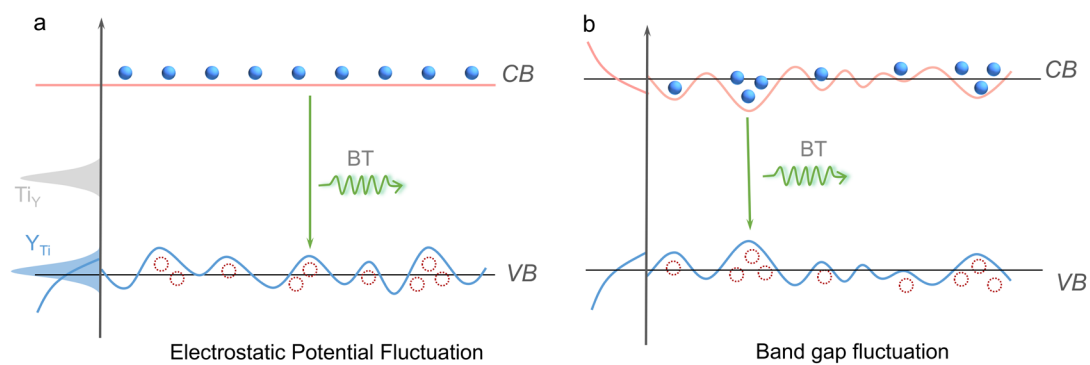


Fig. S11 Schematic diagrams of possible mechanisms of band-tail states transitions in $Y_2Ti_2O_5S_2$. (a), Electrostatic potential fluctuation caused by the random distribution of Y_{Ti} antisites. (b) Band gap fluctuation caused by the random distribution of S_O and O_S antisites.

Table S1 Fitting parameters for the TRPL decay curves measured at low temperature.

	I_1 (%)	τ_1 (ns)	I_2 (%)	τ_2 (ns)	β	$\langle\tau_2\rangle$ (ns)	$\langle\tau\rangle$ (ns)
9 K-1.997 eV (FX _{n=2})	4.1	39.05	95.9	18.82	0.862	20.30	21.07
9 K-1.990 eV (FX _{n=1})	61.8	5.72	38.2	8.78	0.494	17.95	10.39
9 K-1.980 eV (D ⁰ X)	5.1	4.95×10^5	94.9	6.73×10^3	0.409	2.11×10^4	4.53×10^4
15 K-2.003 eV (FC)	2.3	2.34	97.7	0.12	0.675	0.15	0.20

τ_i is the decay time and I_i is the fractional intensity of each decay channel; $\langle\tau_2\rangle$ is the average lifetime of the stretched exponential decay process: $\langle\tau_2\rangle = \frac{\tau_2}{\beta} \Gamma(\frac{1}{\beta})$; and $\langle\tau\rangle$ is intensity-weighted average lifetime of the total decay process: $\langle\tau\rangle = I_1\tau_1 + I_2\langle\tau_2\rangle$

Table S2 Fitting parameters for the TRPL decay curves measured at different temperatures ranging from 60 to 160 K.

Temperature (K)	I ₁ (%)	τ ₁ (ns)	I ₂ (%)	τ ₂ (ns)	β	<τ ₂ > (ns)	<τ> (ns)
60	93.6	0.141	6.4	0.243	0.359	1.12	0.20
80	95.7	0.130	4.3	0.483	0.264	8.46	0.49
100	81.8	0.115	18.2	0.479	0.365	2.09	0.47
120	65.3	0.224	34.7	0.487	0.334	2.89	1.15
140	56.4	0.173	43.7	0.332	0.337	2.15	1.04
160	18.4	0.187	81.6	0.298	0.336	1.74	1.45

τ_i is the decay time and I_i is the fractional intensity of each decay channel; <τ₂> is the average lifetime of the stretched exponential decay process: $\langle \tau_2 \rangle = \frac{\tau_2}{\beta} \Gamma(\frac{1}{\beta})$; and <τ> is intensity-weighted average lifetime of the total decay process: $\langle \tau \rangle = I_1 \tau_1 + I_2 \langle \tau_2 \rangle$

Table S3 Fitting parameters for the TRPL decay curves measured at different temperatures ranging from 180 to 300 K.

Temperature (K)	τ_0 (ns)	β	$\langle\tau\rangle$ (ns)
180	1.07	0.468	2.44
200	2.36	0.617	3.43
220	3.07	0.679	4.01
240	3.54	0.698	4.49
260	4.18	0.719	5.16
280	4.65	0.738	5.61
300	4.89	0.748	5.83

$\langle\tau\rangle$ is the average lifetime of the stretched exponential decay process: $\langle\tau\rangle = \frac{\tau_0}{\beta} \Gamma(\frac{1}{\beta})$.

Table S4 The formation energy ΔH (eV) of isolated point defects in $Y_2Ti_2O_5S_2$ at different chemical potentials A, B, C, D, E, F, and G.

Defect	V_O	V_S	V_Y	V_{Ti}	$O_i(1)$	$O_i(2)$	S_i	Y_i	Ti_i	O_s	S_o	Y_{Ti}	Ti_Y
S rich													
	<i>A: $\mu_Y=-6.09, \mu_{Ti}=-4.94, \mu_S=0, \mu_O=-2.65$</i>												
ΔH_f^x	2.964	3.644	5.555	7.021	3.467	2.666	2.898	6.376	5.308	0.935	1.524	0.789	2.507
	<i>B: $\mu_Y=-6.31, \mu_{Ti}=-5.08, \mu_S=0, \mu_O=-2.51$</i>												
ΔH_f^x	3.104	3.644	5.335	6.881	3.327	2.526	2.898	6.596	5.448	0.795	1.664	0.869	2.427
	<i>C: $\mu_Y=-6.00, \mu_{Ti}=-3.87, \mu_S=0, \mu_O=-3.12$</i>												
ΔH_f^x	2.494	3.644	5.645	8.091	3.937	3.136	2.898	6.286	4.238	1.405	1.054	1.769	1.527
	<i>D: $\mu_Y=-5.82, \mu_{Ti}=-3.87, \mu_S=0, \mu_O=-3.19$</i>												
ΔH_f^x	2.424	3.644	5.825	8.091	4.007	3.206	2.898	6.106	4.238	1.475	0.984	1.589	1.707
S poor													
	<i>G: $\mu_Y=-2.49, \mu_{Ti}=0, \mu_S=-2.54, \mu_O=-5.05$</i>												
ΔH_f^x	0.564	1.104	9.155	11.961	5.867	5.066	5.438	2.776	0.368	0.795	1.664	2.129	1.167
	<i>E: $\mu_Y=-3.90, \mu_{Ti}=-1.8, \mu_S=-1.5, \mu_O=-4.18$</i>												
ΔH_f^x	1.434	2.144	7.745	10.161	4.997	4.196	4.398	4.186	2.168	0.965	1.494	1.739	1.557
	<i>F: $\mu_Y=-5.00, \mu_{Ti}=-2.8, \mu_S=-0.5, \mu_O=-3.74$</i>												
ΔH_f^x	1.874	3.144	6.645	9.161	4.557	3.756	3.398	5.286	3.168	1.525	0.934	1.839	1.457
<p>A, B, C, D, and G are all chemical potential edge points. A, B, C, and D are shown in Fig. 6b and G is shown in Fig. S7. E and F are two points randomly selected within the stable region. The red dashed rectangle highlights the relatively low formation energy of defects under S-rich condition.</p>													