Electronic Supplementary Information (ESI)†

Unveiling the Role of Surface Iodine Vacancies in CsPbI₃ Perovskite:

Carrier Recombination Dynamics and Defect Passivation Mechanisms

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S1. Computational Details

1.1 Coupled kinetic equations

Table 1 in the text summarizes the carrier recombination rates $1/\tau$ (described by the symbol k) of pairwise transitions in the perfect surface, various surface V_I defects, and the systems after $HCOO^-$ passivator, obtained by the exponential fitting. In order to systematically evaluate the total lifetime of excited carriers in various systems, it is necessary to consider participating in the whole carrier transition process. Therefore, we construct a dynamic model to describe the dynamic behavior of carrier coupling in these systems. The detailed description of carrier recombination/trapping dynamics is as follows:

(1) For the perfect and resonant defect systems, as well as the defect systems passivated by $HCOO^-$: carrier recombination between electrons in CBM and holes in VBM, see process 2 in Fig. 5a, $k_{(CBM \to VBM)}$.

(2) For systems with defective states within the band gap: carrier recombination between electrons in CBM and holes in VBM, see process 2 in Fig. 5b, $k_{(CBM \to VBM)}$; electrons trapping by DS (process 3, $k_{(CBM \to DS)}$); holes trapping by DS (process 4, $k_{(VBM \to DS)}$).

Thus, for the perfect surface, the defective systems, as well as the defect systems passivated by $HCOO^-$, their coupled kinetic equations are:

$$\frac{d[VBM]}{dt} = - k_{(CBM \to VBM)}[VBM] \tag{1}$$

$$\frac{d[CBM]}{dt} = k_{(CBM \to VBM)}[CBM] \tag{2}$$

The coupled kinetics equations for the defect systems on the subsurface are:

$$\frac{d[VBM]}{dt} = - (k_{(CBM \to VBM)} + k_{(CBM \to DS)})[VBM] \tag{3}$$

$$\frac{d[DS]}{dt} = k_{(CBM \to DS)}[CBM] - k_{(DS \to VBM)})[DS] \tag{4}$$

$$\frac{d[CBM]}{dt} = k_{(CBM \rightarrow VBM)}[VBM] + k_{(DS \rightarrow VBM)})[DS] \tag{5}$$

Where [VBM], [DS] and [CBM] are populations of the VBM, defect and CBM states, respectively. The overall lifetime (or recombination rate) at CBM for all systems are obtained by the exponential fitting, and results are shown in Table 1 and Fig. 5(e-f).

Here, we use V_I defects located at the outermost layer and the subsurface Pb-nondimer structures as examples to describe the carrier relaxation and trapping processes, see Table 1 and Figs. 5(a-b). The carrier lifetime for the pairwise states is obtained by the DISH method, and the corresponding fitting results are shown in Figs. S4-S7.

1.2 Computational process of absorption energy

The absorption energy (E_{adsor}) of passivator molecular (HCOO⁻) for CsPbI$_3$ perovskite surface is calculated as:

$$E_{adsor} = E_{perov + mol} - E_{perov} - E_{mol} \tag{6}$$

where $E_{perov + mol}$, E_{perov}, and E_{mol} represent the energy values of the passivated perovskite system, the bare perovskite, and the passivating molecule, respectively.
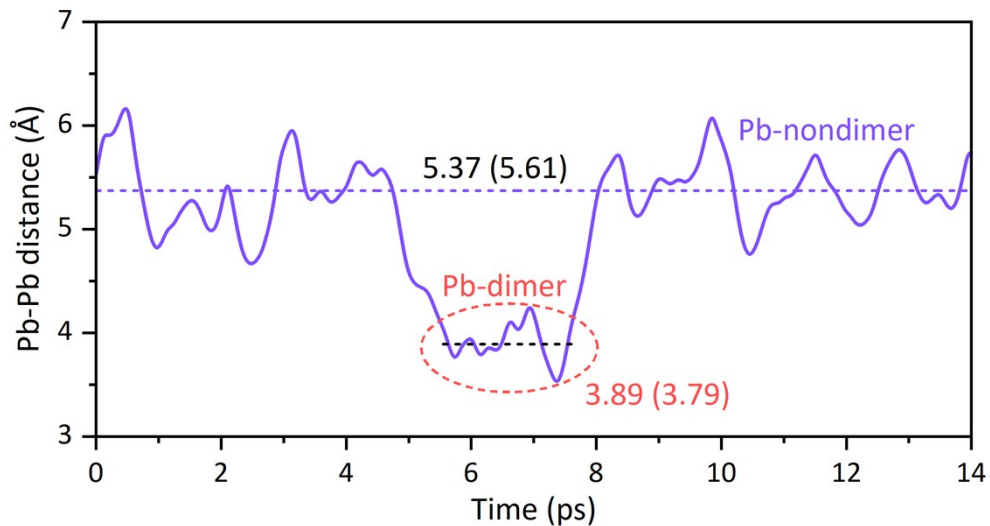
S2. Supplementary Figures

Fig. S1. Evolution of Pb-Pb distances around V_I defect on the subsurface. These data represent the standard average Pb-Pb distances along MD trajectory, while the values in parentheses are the Pb-Pb distance in the optimized ground state structures. The Pb-dimer configuration shows the temporary stability, which reveals that V_I defect on the subsurface is mainly Pb-nondimer configuration.
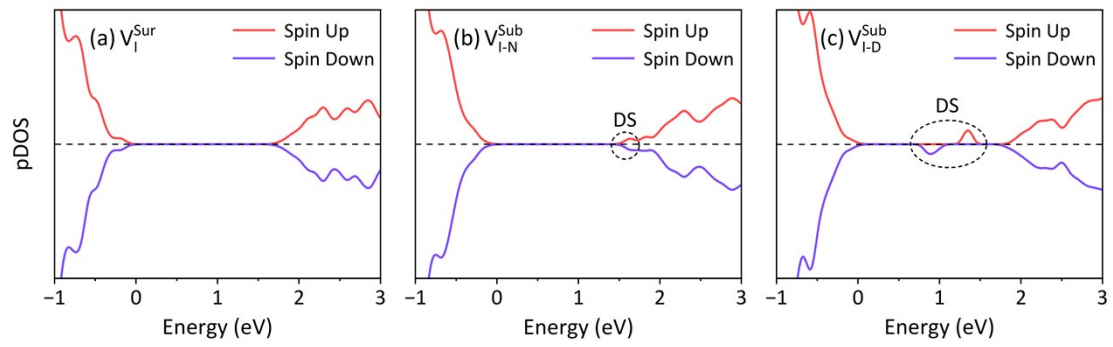
Fig. S2. Spin-polarized calculations of electronic structures on the (a) V^{Sur}_{I}, (b) V^{Sub}_{I-N} and (c) V^{Sub}_{I-D} defects, including the spin-up and spin-down results. The VBM level is set to zero.
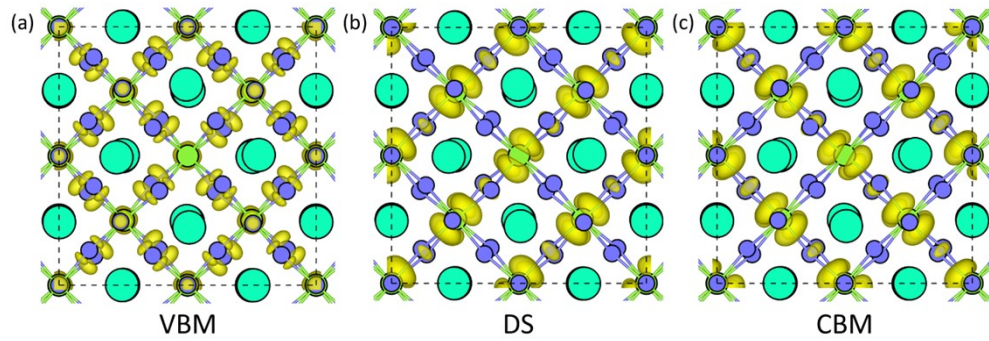

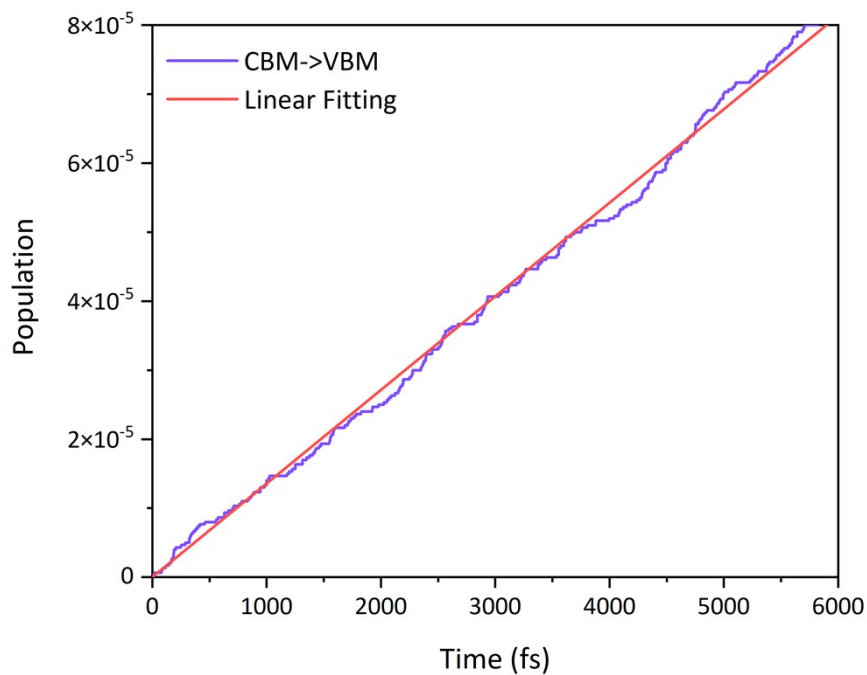**Fig. S3.** Charge density distribution of V^{Sur}_{I} defect, including the VBM, defect state (DS), and CBM.

Fig. S4. Population evolution of CBM state due to the relaxation from CBM to VBM in the surface V_I defect localized at the outermost layer. The fitting function is $f(t) = t/(7.37 \times 10^7)$.
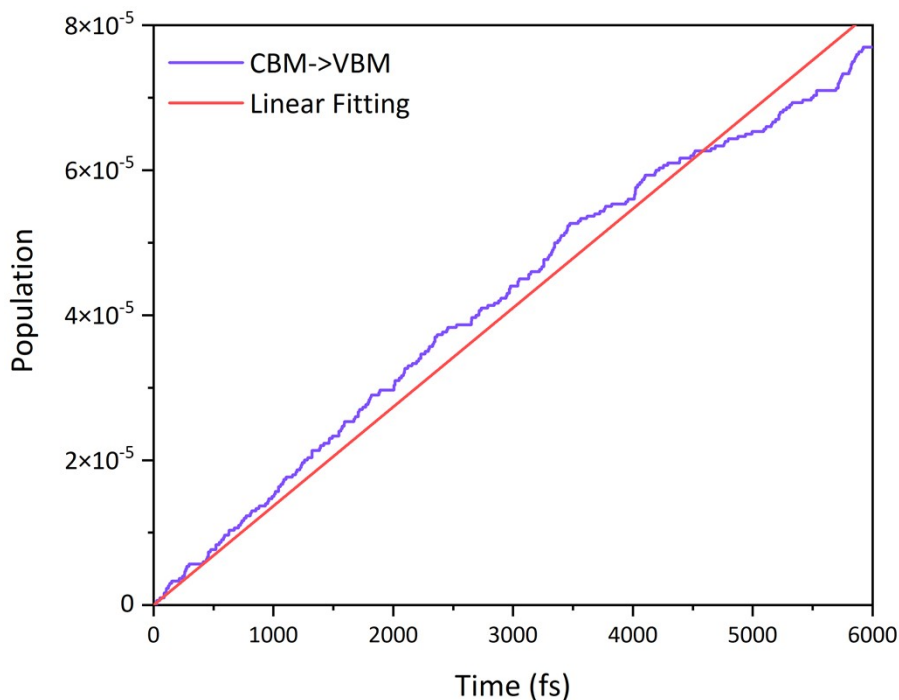

Fig. S5. Population evolution of CBM state due to the relaxation from CBM to VBM in V_I defect with Pb-dimer configuration localized at the subsurface layer. The fitting function is $f(t) = t/(7.31 \times 10^7)$.
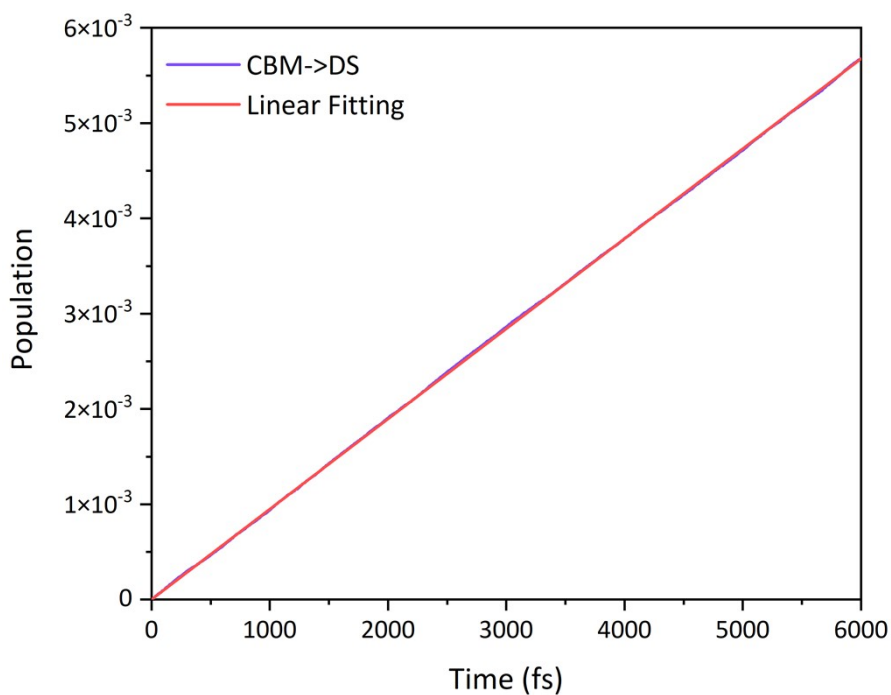

Fig. S6. Population evolution of DS during electron trapping in the V_I defect with Pb-dimer configuration localized at the subsurface layer. The fitting function is $f(t) = t/(1.05 \times 10^6)$.
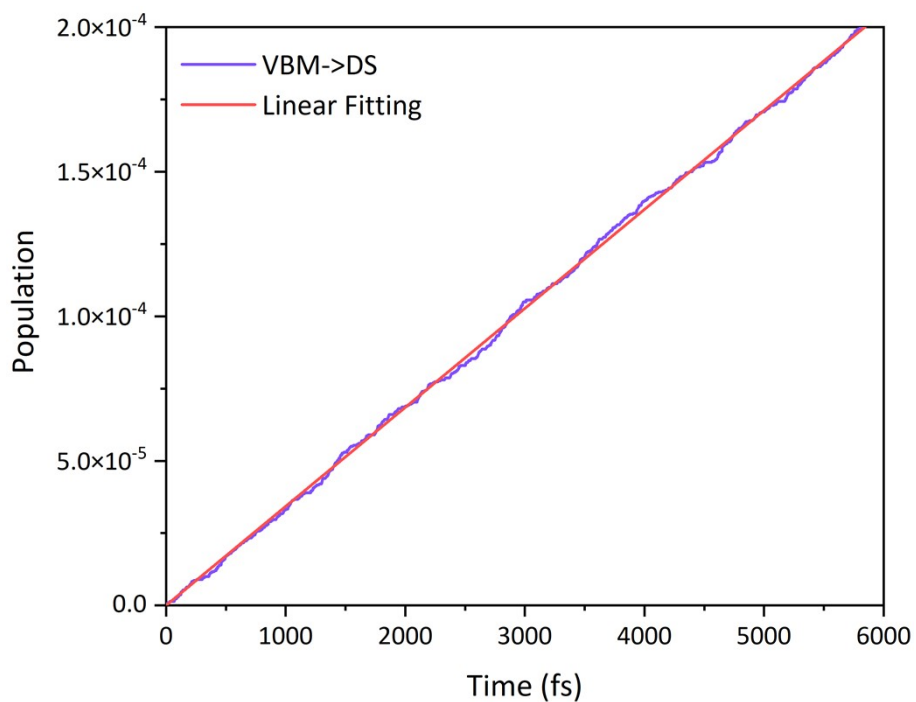
Fig. S7. Population evolution of DS during hole trapping in the V_I defect with Pb-dimer configuration localized at the subsurface layer. The fitting function is $f(t) = t/(2.92 \times 10^7)$.
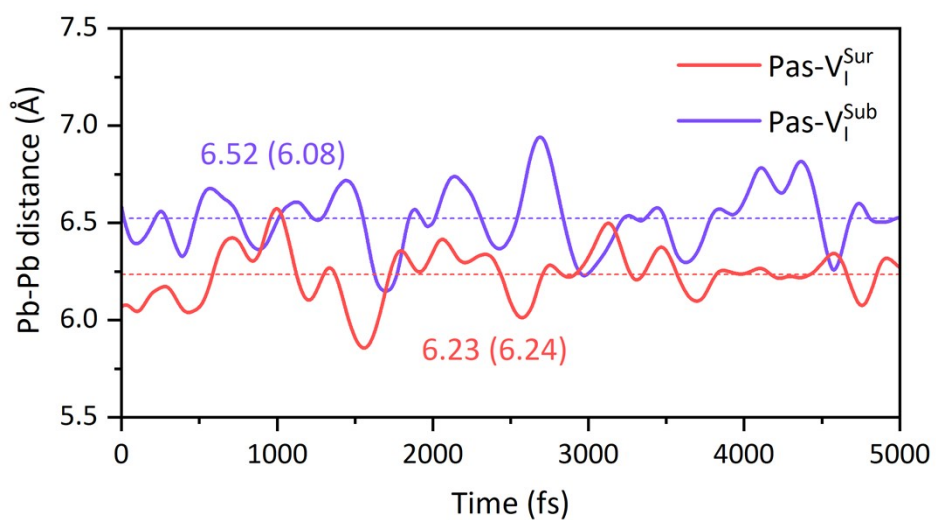

Fig. S8. Evolution of Pb-Pb distances after passivation of V_I on the perovskite surface with HCOO$^-$. These data represent the standard average Pb-Pb distances along MD trajectory, while values in parentheses are the Pb-Pb distance in the optimized ground state structures.