Electronic Supplementary Information (ESI)

Unusual defect properties of the one-dimensional photovoltiac semiconductor selenium

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This file contains Calculation Methods, Fig. S1-S5, and Table S1.

Calculation Methods

All the crystal structures, formation energies, and electronic structures were calculated using the density functional theory with the projector augmented plane-wave method, as implemented in the Vienna Ab initio Simulation Package (VASP).[1,2] The crystal structures and formation energies were calculated using the Perdew-Burke-Ernzerhof (PBE) generalized gradient approximation (GGA).[3] The cutoff energy for the plane wave is set to 450 eV. The hybrid functional in the Heyd-Scuseria-Ernzerhof (HSE) form with a fraction $\alpha = 25\%$ of Hartree-Fock exchange was used for calculation of the electronic structure.[4,5] The energy criterion is set to 10^{-5} eV in iterative solution of the Kohn-Sham equation. All the structures are relaxed until the residual forces on the atoms are less than 0.02 eV/Å.

Several supercells containing different numbers of Se atoms were built, and the corresponding formation energies of two intrinsic point defects were calculated, as shown in Table S1. Although the differences in the formation energies and the transition energy levels of the two defects between the different supercells are negligible, we use a $3 \times 4 \times 4$ supercell (144 atoms) here to achieve more accurate results, considering the high computational cost of HSE06. For the electronic structure calculations of intrinsic point defects, the first Brillouin zone was sampled using a Monkhorst Pack scheme on a $3 \times 3 \times 3$ mesh.
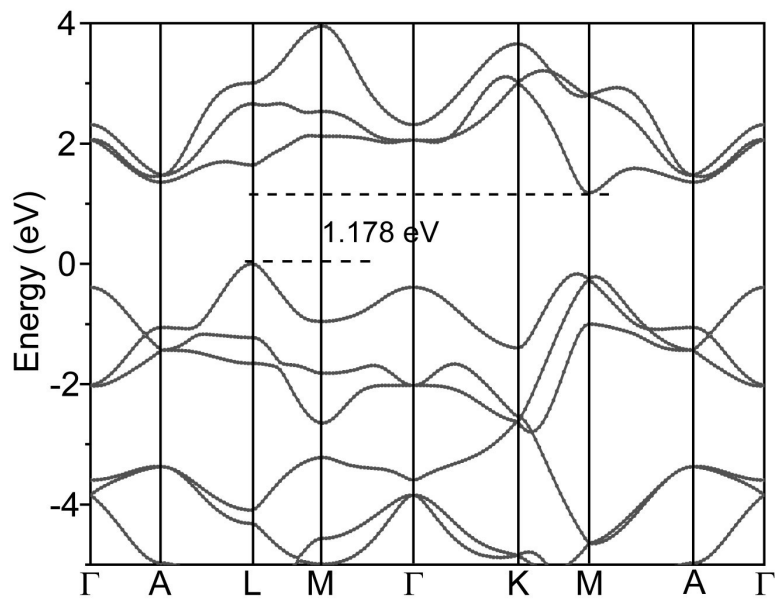
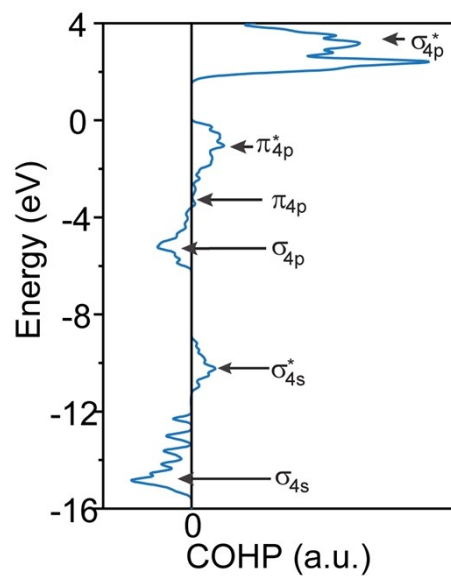**Fig. S1** Band structure of t-Se calculated using the PBE level.
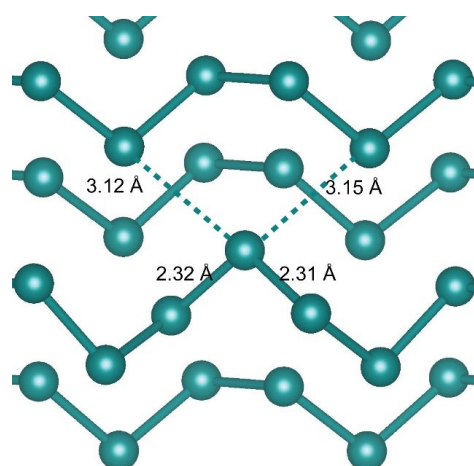
Fig. S2 Calculated COHP of t-Se.

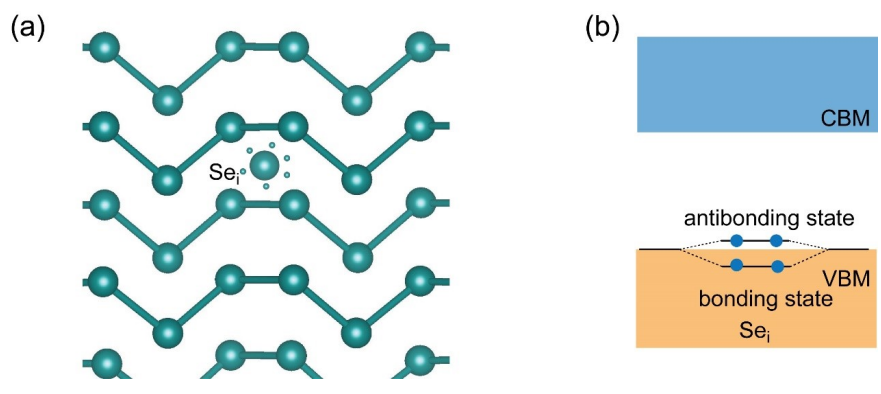**Fig. S3** The crystal structure of optimized Se$_i$.

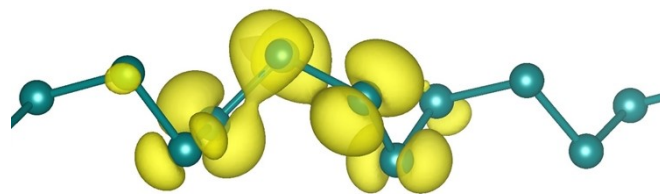**Fig. S4** Schematic diagram of (a) Se_i and (b) its defect level.

Fig. S5 Contour plot of the norm-squared wave function of the defect state of Se_i.

Table S1 Formation energies and transition energy levels of two defects in different supercells.

Supercell	Number of atoms	Formation energy (eV)		Transition energy levels of two defects above VBM (eV)	
		V_{Se}	Se_i	V_{Se}	Se_i
$3 \times 3 \times 3$	81	1.42	1.68	0.18	0.20
$3 \times 3 \times 4$	108	1.42	1.67	0.18	0.21
$3 \times 4 \times 4$	144	1.41	1.67	0.19	0.21

References

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